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1.0 QUALITY ASSURANCE OBJECTIVES

QA objectives provide a set of recognized parameters to monitor and to quantify performance of an analytical measurement. This document provides specific criteria for QA objectives to ensure that laboratories engaged in compliance activities supporting the RL maintain a uniform standard of performance.

1.1 DATA QUALITY OBJECTIVES

The primary responsibility for identifying data quality requirements lies with the client or data user. The client or data user is also responsible for communicating this information to the organization or staff responsible for performing the work. The communication process should be such that it allows the laboratory to understand and successfully meet client data quality requirements and comply with applicable regulations, basic information about the nature of the sample(s) and the use of the data should be discussed and agreed upon by the laboratory and the client before sample collection. This information should be provided through a formal DQO process (see Appendix A). In the absence of a documented DQO process, as a minimum, the laboratory and the client shall agree upon the required precision, accuracy, and sensitivity (e.g., IDL, MDL, MDC). Also, the following sample-specific criteria should be provided or agreed upon and documented before the laboratory begins work:

Applicable regulatory requirements such as chain-of-custody, holding times, and QC specifications

Process knowledge, sample source, and sample conditions known to the client that could impact the laboratory worker's safety

Handling of radioactive samples in the transport process and in the laboratory

Estimated number and matrix of samples

Sample handling relative to a specific sample or matrix

Procedures and analyte lists for sample analysis -- the analyte list should also specify whether or not tentatively identified compounds are required

QC sample frequency, type, and acceptance criteria

Expected dates of sample receipt, sample preservation, delivery methods, storage and container types and volumes, and holding times by method

Format, content of sample analysis reports, and format of electronic data deliverables if requested

Turnaround time (from date of sample receipt to date of data delivery) in the laboratory

Name, address, telephone number of client, and laboratory contacts responsible for the project, and information to establish electronic data transfer (e.g., type of software, file format)

Methods for reporting, resolving, and documenting anomalies and nonconformances from sample receipt to final reporting to the client -- for example, either stop work or revision to the original work requests could be used for non-conforming samples upon their submittal to the laboratory

Return of samples and disposition of waste.

The laboratory shall have a system to notify and explain to all staff performing work for the client any unique requirements. Unique requirements are those that differ from the procedures described in this document and in the laboratory procedures.

The laboratory shall notify the client when situations, such as anomalies and nonconformances, occur.

The laboratory shall have a process for documenting resolution of client complaints or issues. The process shall include documenting the complaint or the issue, the client contact, and the date the contact was made. All subsequent information that resolves the complaint or issue shall be maintained by the laboratory. The laboratory shall track the complaint or the issue from receipt to resolution.

1.2 CLIENT DATA QUALITY REQUIREMENTS

Five parameters are often used by the client to define project data quality requirements. These are precision, accuracy, completeness, comparability, and representativeness. Of these, the precision, accuracy, and representativeness have direct impacts on data quality (see Section 6.0 for limitations associated with precision and accuracy). The client is responsible for ensuring that adequate sample material is available and that appropriate sampling techniques are administered to meet their DQOs. The laboratory is responsible for using proper protective sample handling protocols. The laboratory and the client share responsibility for selecting appropriate sample preparation and analytical technique. The precision and accuracy requirements shall be agreed on by the laboratory and the client and should be based on the error tolerances of both the sampling and the analytical effort.

1.2.1 Precision

Precision represents a measure of the degree of reproducibility of measurements under prescribed similar conditions. Sample precision is calculated on the basis of duplicate analyses. Acceptance criteria shall be established for each analyte and each analyte method and shall be agreed upon by the laboratory and the client.

1.2.2 Accuracy

Accuracy represents the degree to which a measurement agrees with an accepted reference or true value. Sample accuracy is expressed as the percent recovery of a spiked sample. Acceptance criteria shall be established for each analyte and each analyte method and shall be agreed upon by the laboratory and the client.

1.2.3 Comparability

Comparability is the confidence with which one data set can be compared to another. For each analyte, comparable precision and accuracy depend on the method and sample matrix. To be comparable, similar precision, accuracy, and detection limits shall be achieved on samples with similar matrices using similar methods. Factors such as analytical method selected, detection limits or uncertainty, precision, accuracy, and matrix effects should be considered when data are to be compared between multiple laboratories. Furthermore, a split sample or a known standard shall be used for comparability of different methods.

1.2.4 Completeness

Completeness is a measure of the amount of usable and/or valid data obtained from a measurement system compared to the total amount of data requested. Completeness can be used to evaluate the amount of data produced that meets the client's requirements (e.g., accuracy, precision). In some cases, data may not meet all the requirements but may still be used for qualitative information as an indicator of the presence or absence of a parameter. A clear definition of completeness based on the types of qualification allowed should be agreed on by the laboratory and the client. Developing a requirement for critical samples that differ from other samples may also be useful.

1.2.5 Representativeness

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, a parameter variation at a sampling point, a process condition, or an environmental condition. Representativeness of a population or an environmental condition depends heavily on sampling and is addressed in other documents (which are not in the scope of this document). Analytical data should not be taken as the sole indicator of representativeness of the sample process condition. The methods should be assessed after accumulation of sufficient data to represent the same population.

The laboratory is responsible for handling and preparing the sample properly to maintain representativeness of the sample. Representativeness may be obtained by proper homogenization or subsampling. If different phases are apparently visible in the sample, the laboratory should consult with the client to determine subsampling and homogenization needs.

If subsampling is needed, the data quality requirements should be re-evaluated to determine if subsampling impacts the ability to meet representativeness requirements and if a different methodology is required for preparation and analysis. Both the laboratory and the client should recognize that representativeness of the sample may be impacted by difficulty in, or inability to, achieve homogeneity.

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2.0 SYSTEMS QUALITY ASSURANCE

A number of systems exist within a laboratory. These systems need to function properly to produce and document the high level of quality needed in the final product. These systems are the software systems, administrative systems, technical systems, and physical facilities systems. Administrative controls shall be established for each system.

Technical systems and physical facilities are discussed in this section. Software systems are discussed in Volume 1, Section 7.0.

2.1 TECHNICAL SYSTEMS

Technical systems assure that the techniques used are applicable and properly applied. These systems include sample exchanges, standards programs, control of standards and reagents, data reduction and reporting, data verification and validation, and technical audits. Procedures for documenting the above systems shall be established.

2.2 PHYSICAL FACILITIES SYSTEMS

Proper facility design and maintenance can help alleviate problems associated with data generation. The following issues, at a minimum, should be addressed:

Ventilation, with air exchange rates, and pressure differential between work area, suitable working environment (e.g., lighting, temperature control), stable power sources and radio frequency shielding.

Adequate space for laboratory functions so that laboratory activities do not adversely affect analyses.

Specialized equipment, such as an acid hood or glovebox, where required.

Water purification (see Section 6.1.1).

Preventive maintenance schedules for equipment (see Volume 1, Section 9.0).

Proper maintenance to prevent contaminating vacuum systems.

Adequate storage with temperature control and temperature monitoring to provide for

security of samples and to prevent contamination, degradation or misidentification of samples.

Adequate storage areas for reagents, solvents, standards, and reference materials to prevent cross contamination or degradation.

Adequate facilities for collection, storage, and disposition of sample wastes (with facilities operated to minimize environmental contamination).

Waste management facilities to comply with applicable federal, state, and local regulations.

3.0 SAMPLE CUSTODY AND HANDLING

This section identifies requirements for chain-of-custody to be maintained between the sample collection and the laboratory receiving area, and specifies requirements for internal custody in the laboratory. Internal custody refers to maintaining custody as the sample is removed from storage and dispersed within the laboratory for analysis. Internal custody is maintained until final disposition or return of the sample to the client. The scope of this document is limited to the custody requirements beginning with laboratory sample receipt.

3.1 CHAIN-OF-CUSTODY DEFINITION

The purpose of the chain-of-custody is to document sample possession and to demonstrate that the sample was maintained in a controlled and unaltered state. This demonstration supports the interpretation of the sample results and may be required in legal proceedings, as well as for a number of other purposes.

Custody in the laboratory is defined as secured to prevent tampering and may be accomplished by having the sample be in one of the following situations: 1) in actual physical possession, 2) in view of the sample custodian after being in physical possession, 3) in a locked area, or 4) in a designated secured area (accessible only to authorized personnel).

3.2 HOLDING TIMES

Many analytes regulated under environmental statutes (e.g., the CERCLA, and the *Clean Water Act*) require adherence to holding time requirements. Regulatory holding time begins at sample collection. Some regulatory holding times include collection through final analysis; others segregate the time between collection through preparation, and preparation through analysis. The EPA has set maximum holding times for most analytes regulated under the RCRA (EPA, SW-846). The aqueous holding time requirements are consistent with those in the *Clean Water Act* in 40 CFR 136.

The laboratory and the client shall agree upon the necessity of applying regulatory holding times before sample collection. The client shall be responsible for the timely delivery of samples to the laboratory enabling the laboratory to meet holding time requirements. If the laboratory is unable, for any reason, to meet prescribed holding times, the laboratory shall notify the client in writing as soon as possible.

3.3 SAMPLE RECEIVING

The laboratory shall have a procedure, or series of procedures which address sample receipt. The

following actions shall be addressed in the laboratory procedure(s):

Document transferring samples to the laboratory by a common carrier. A copy of the shipping document shall become part of the permanent laboratory record.

Verify that the outermost sample container(s) is not damaged.

Verify that the outermost sample seal(s) is intact, if present.

Assure that radiation control procedures are followed for receipt, when applicable.

Verify that the chain-of-custody documentation, if received from the carrier, is accurate, complete, and legible; the documentation should include descriptions of any deficiencies identified by previous custodians as well as the following information:

- Client name.
- Project name or number.
- Client sample number.
- Date and time of sampling for each sample.
- Container types, and sizes and number of containers.
- Short description of sample, including matrix and designation as sample or QC.
- Analyses requested (or a reference to the analyses).
- Preservation (material used, or "none",or "N/A" if not applicable).
- Date and time of relinquish and receipt.
- Signatures of those persons relinquishing and receiving.

Verify the temperature of the cooler when it is received where specified by the procedures or protocols, and note any deviations.

Verify that the collection date and date of laboratory receipt are within method- or project-specific holding time requirements.

Notify laboratory staff as soon as possible when the sample holding time is less than 48 hours.

Verify that the client's sample numbers on the chain-of-custody match those on the sample containers.

- Evaluate the condition of sample containers.

- Note anomalies either on the custody form or on nonconformance documentation.

When specified in client agreements, the laboratory shall provide for notice, within 24 hours, of samples received. Notice may be by telephone, facsimile, or electronic mail.

Laboratory procedure(s) shall provide for timely notification to the client of any nonconformance which will impact the laboratory's ability to meet agreed upon data quality requirements before proceeding with further work, by telephone, facsimile, or electronic mail. The laboratory shall maintain the documentation supporting such notifications, which may include copies of the telephone logs, facsimiles, or electronic mail. Nonconformance notification and client responses shall be documented, tracked through closure, and kept on file in the laboratory.

In the event that prompt client response (within two business days) is not received to a notification of nonconformance, the laboratory can proceed at its discretion to analyze the samples. All actions and decisions must be documented in the project file, and include a summary of the nonconformances and corrective actions in the narrative accompanying the final report.

When sample receipt is completed and samples are accepted for analysis, the laboratory shall initiate internal chain-of-custody in accordance with Section 3.5 and begin analytical activities.

3.4 SAMPLE LOG-IN AND TRACKING

Upon receipt of samples in the laboratory, the following shall be completed as part of the sample log-in and tracking process, and shall be addressed in appropriate laboratory procedures.

Having accepted the samples, the laboratory shall maintain custody of the samples during the laboratory log-in and sample distribution processes. The samples shall be secured in a designated refrigerated or other storage location as appropriate for the sample container and material type.

The laboratory shall ensure that the records documenting possession and transfer are properly completed and placed in the laboratory records system.

The laboratory shall maintain a cross-reference to correlate the laboratory's sample identification to the client's sample identification.

Each sample or subsample shall be given a unique identifier regardless of its resample status. Every sample, sample replicate, subsample, and sample extract shall be labeled in a manner that allows traceability to the parent sample number.

Information related to storage, preservation, holding time, and requested analysis shall match work-authorizing document (e.g., tank characterization plan).

Any safety hazards communicated by the client shall be documented and communicated to the laboratory staff.

A declaration of the radiation level shall accompany those samples that contain radioactive materials.

A system shall be in place to allow tracking of samples and holding times. The system shall allow the laboratory to assess if holding times shall be met or exceeded, and to assess the number of samples available for analysis.

3.5 LABORATORY INTERNAL CHAIN-OF-CUSTODY

The laboratory approach taken to address internal chain-of-custody of samples shall be documented and implemented through approved internal procedures. Once samples are in the laboratory, sample custody shall be controlled. The location of all samples and the person in control of the samples shall be traceable from the time samples are received at the laboratory until final disposition. Traceability within the laboratory may be electronic, based on personnel bar codes, passwords, or other secure techniques.

In a laboratory restricted to authorized personnel only, the entire laboratory is considered a secured area, provided the laboratory has developed and implemented procedures that addresses laboratory security.

Shipping records shall be maintained. If a chain-of-custody failure is detected, the client shall be contacted for resolution.

3.6 SAMPLE DISPOSITION

The sample disposition procedure shall include the following:

return of samples to the client or dispositioning through other laboratory waste management systems.

maintenance of records that identify the date and method of sample disposition.

provisions to ensure all federal, state, and local disposal regulations have been met.

provisions for sample archiving.

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4.0 CALIBRATION

This section describes calibration and/or activities associated with calibration requirements for laboratory measurement systems and specifications for standards that are used for calibration. The performance of the laboratory measurement system, in general, is controlled through calibration and monitored by continuing verification of calibration.

Chemical measurements are made using a system that includes sample handling and measurement processes. All aspects of the measurement process should be calibrated. Ancillary data on such matters as temperature, pressure, humidity, particle size, volumetric capacity, mass, and flow rate may be needed as well, requiring accurately calibrated instrumentation for their measurement. Accordingly, any of the instruments, standards, and methods used for these purposes should be calibrated to assure that their accuracy is within acceptable limits.

Requirements for calibration are different between radionuclide, inorganic, and organic analyses because of instrumentation characteristics and stability. This is primarily due to long-term (radiochemical) versus short-term (inorganic and organic) system stability. The detectors used within these chemical classes also have different calibration requirements based on their operating characteristics. It is inappropriate and unnecessary to impose the more frequent calibration requirements of inorganic and organic calibration and initial calibration verification on radiochemical procedures. Care must also be taken within a class of analysis to apply method-specific procedures properly or risk inaccurate calibration. The requirements between and within chemical classes of analysis are discussed below.

If more or less stringent requirements are necessary to meet project objectives, the variances shall be implemented according to data quality requirements agreed to and documented between the laboratory and the client (Section 1.0).

4.1 CALIBRATION RECORDS

The laboratory shall keep a record of raw calibration data for all methods. Calibration records (initial calibration, initial calibration verification, and continuing calibration verification) shall include the raw calibration data, associated reports, date of analysis, and analyst's name or initials, at a minimum. Calibration data shall be traceable to the standards used. All samples analyzed shall be traceable to the calibration under which the results were produced. Sample analysis can only proceed when measurement systems are accurately calibrated. These records shall be maintained according to Volume 1, Section 6.0.

4.2 BALANCES, THERMOMETERS, AND PIPETTES

Calibration records of measurement devices such as laboratory balances and thermometers for critical mass and temperature measurements shall be maintained. All analytical balances shall be calibrated annually, at a minimum, by an approved metrology organization. An approved metrology organization is one that has been evaluated and selected on the basis of specified criteria consistent with industry standards for the calibration of balances. These records shall contain the date of calibration, initials of the person performing the calibration, the identity of the device or serial number, and the date the calibration expires. This information shall be affixed on or near the balance. Acceptable balance calibration shall be verified and documented daily when in use. The accuracy of thermometers and thermocouples used for critical temperature measurements (e.g., refrigerator temperature for sample storage, total dissolved solids analysis) shall be verified annually by comparing readings of such devices with the readings of a National Institute of Standards and Technology traceable factory-certified thermometer. If radiological conditions limit this capability, then the thermometer should be checked at the ice point.

It is considered good laboratory practice that mechanical pipettes used for critical measurements be verified to ensure acceptable performance. Daily, before use, single-delivery volume checks should be performed and documented.

4.3 GENERAL REQUIREMENTS FOR STANDARDS

The following standard specifications shall be used unless otherwise specified in Section 4.4.

Standards used for calibration of measurement systems shall be traceable to a nationally or internationally recognized standard agency source or measurement system if available. A program for verifying and documenting the accuracy and traceability of all working standards against appropriate primary grade standards or the highest quality standards available should be routinely followed.

Standards used for calibration shall be accompanied by a certificate or record that includes the vendor, lot number, purity, date of preparation and/or expiration, and concentration or activity of the standard material. At a minimum, the following information shall be maintained on standard preparations and if possible placed on the label:

Name of preparer

Date prepared

Standard identification

Dilution performed

Final concentration or activity

Expiration date or shelf life (if applicable).

When recognized standard material is unavailable or its purchase is impractical, the laboratory should attempt to purchase standard material from a reliable source. The laboratory shall have procedures in place to determine the acceptability of such materials.

4.4 CALIBRATION OF LABORATORY MEASUREMENT SYSTEMS

The calibration process correlates instrument response to an established concentration or characteristic. Calibration procedures shall be established by the laboratory and shall consider the manufacturer's recommendations and the requirements specified in this section. Specific requirements or considerations for calibration and calibration standards used for radiochemistry, inorganic, organic and physical testing laboratory measurement systems are defined in Sections 4.4.1, 4.4.2, 4.4.3, and 4.4.4, respectively.

The initial calibration verification checks the accuracy of the calibration and the standards used for that purpose. A level of independence shall exist between the materials used for calibration and for initial calibration verification when such materials are available. When an independent source is not available, the laboratory should attempt to purchase an alternate lot of the same material.

The continuing calibration verification checks the stability of the original calibration over time. This standard may be from the same source as that used for either calibration or initial calibration verification.

The minimum requirements of calibration, frequency, and acceptance criteria for laboratory measurement systems are presented in Tables 4-1 through 4-9.

Records associated with instrument calibration and control shall identify the following:

- Test type
- Date of test
- Name of person performing the test
- Results and their acceptability
- Corrective actions taken when unacceptable

The laboratory is required to take corrective action when measurement systems fail calibration QC criteria as demonstrated by the procedures discussed in Section 5.0. When recalibration is required at an unusual and/or increasing frequency, see Volume 1, Section 5.0 for corrective actions.

4.4.1 Radionuclide Analysis

Radionuclide analysis is defined as the measurement of nuclear decay through counting alpha, beta, and/or photon emissions. There are many different kinds of counting instruments used to measure these emissions. Examples include,

Alpha
- silicon surface barrier
- gas-flow proportional
- ZnS scintillation

Beta
- gas-flow proportional
- liquid scintillation

Photon
- gamma spectrometers
- low-energy (X-ray) spectrometers

These detector systems are used in support of a variety of analytical needs ranging from screening to isotope-specific identification and quantification.

Four main counting equipment categories are described in Tables 4-1 through 4-4, alpha and beta analysis using gas-flow proportional counting, gamma spectrometry, alpha spectrometry, and beta spectrometry using liquid scintillation counting. Other counting systems are available to radiochemists; the calibration concepts described herein are applicable to these other systems as well.

There are several fundamental aspects to calibration of counting equipment. These are:

Energy of emitted radiation
Isotope activity
Sample geometry
Attenuation
Interferences.

All of these fundamental aspects must be known in order to effect an appropriate and accurate calibration regardless of the counting instrumentation being calibrated.

Ideally, detectors should be calibrated using the same isotopes as might be encountered in samples since the energy of the emitted radiation strongly effects the efficiency of both beta and gamma detectors.

The isotope(s) used in calibration must have relevance to the emission type and energy of the analyte to be determined. For example, a ^{99}Tc standard is the optimum choice for calibrating a scintillation counter used for ^{99}Tc analysis; ^{14}C is acceptable for the LSC calibration for ^{79}Se as there is no standard source of ^{79}Se available and the β^- energies are comparable. Calibration of photon detectors can be effected in one of two ways, depending on the analytical need. Generally, gamma detectors are calibrated with several isotopes representing a wide range of gamma energies. These calibration curves support general screening of gamma-emitting radionuclides. Gamma detectors may also be useful for single isotope determinations in which case a single point calibration may be utilized. An example of this is a ^{85}Sr calibration for determining Sr radiochemical yields using ^{85}Sr tracer.

The isotope activity in the calibration standard should provide sufficient counts such that random counting statistics are not significant. This can be managed by adjusting the isotope activity and the counting time of the standard.

Sample geometry is critical to detector calibrations. The geometry used for calibration must be reproducible for samples. Geometry includes sample shape/size, homogeneity, and distance from the detector. Alteration of any one or more of these factors will affect the detector counting efficiency and thus the instrument response.

Attenuation of radiation affects all detector types. Attenuation is attributable to a variety of conditions including mass loading on planchets for α/β counting, sample density in the case of photon counting, and quenching effects in the case of liquid scintillation. Where the attenuation is not fundamentally corrected in the calibration (e.g., constant density/matrix between samples and standards), an attenuation calibration will need to be performed. Examples of this include developing quench curves for liquid scintillation and mass calibration curves for α/β counting.

Interferences are often a fundamental problem in counting and can occur during the calibration. These interferences need to be controlled or managed. Examples of interferences are coincident summing of gamma spectral photons and peak tailing in alpha spectrometry (especially in the case of coprecipitation). Gamma coincident summing cannot be avoided, especially with high-efficiency detectors in close sample geometries, thereby making it difficult to obtain smooth efficiency vs. gamma energy curves. In the worst cases, single isotope calibrations are strongly preferred. However, at lower efficiency geometries, the effect may be negligible. Tailing interferences in alpha spectrometry are controlled by performing a peak-fitting routine.

Radiation detection instruments are generally very stable and instrument response can remain constant over a period of years. Calibration standard preparation is often a lengthy process along with the instrument calibration. A detector calibration may take days and remain valid for years. Counter control standards (Section 6.3.3) are measured periodically to confirm calibration stability.

Table 4-1. Minimum Requirements of Calibration, Background, and Counter Control for Alpha and Beta Counting.

Calibration Requirements	Calibration Parameters and Standards[a]	Criteria	Corrective Actions	Frequency
Calibration	Plateau checks as applicable Count one standard over a range of voltage in increments	Plot voltage versus counting activity to estimate proper operating voltages for α and/or ß counting	Set instrument at plateau voltage Investigate the system if cross talk criteria fail	After repair or major maintenance if control of system cannot be re-established
	Cross talk or sensitivity[b] as applicable Measure α count rate from a ß source, and ß count rate from an α source	Cross talk of α in ß: less than 10% Cross talk or sensitivity of ß in α: less than 1%	Investigate the system	
	Counting efficiency to calculate activity in sample Count at one known level for each counting geometry at the applicable energy range	Counting error 1% Establish a curve for efficiency versus mass loading		
	Weight of solids[c] to calculate sample activity when mass loading occurs			
Background counting	Count detector background. Use contamination-free clean planchet.	Establish a background count rate value for total α and total ß[d]	As needed to meet data quality objectives	One per day as the system is used

Table 4-1. Minimum Requirements of Calibration, Background, and Counter Control for Alpha and Beta Counting.

Calibration	Calibration	Criteria	Corrective Actions	Frequency

Requirements	Parameters and Standards			
Counter control or control standard	Use a reliable source	Control limits: three sigma or ± 3%, whichever is greater	Investigate. Recalibrate, if necessary	One per day as the system is used.

Notes:

[a]See Section 4.4.1 for calibration standards requirements, as applicable for the technique used.

[b]When cross talk has an impact on data reduction.

[c]When mass loading is applicable.

[d]At a minimum, the most recent background and its error obtained from the counting system should be used for background substraction. More thorough means (e.g., 10-point running average background) for determining the appropriate background rate and its error may be appropriate for particular situations, and their uses shall be left to the discretion of the radiochemist

Table 4-2. Minimum Requirements of Calibration, Background, and Counter Control for Gamma Spectrometry.

Calibration Requirements	Calibration Parameters and Standards[a]	Criteria	Corrective Actions	Frequency
Calibration	Detector energy calibration Counting efficiency[b] Matrix- and geometry-specific	No specific criteria, depending on total channel and range of energy of desired nuclides Span energy range of nuclides of interests	Not applicable Not applicable	After repair or major maintenance if control of system cannot be re-established
Background	Count detector background to establish background level	Represents the background for the time when the sample is counted[c]	As needed to meet data quality objective	Minimum of every other week or after analytical run whichever is longer
Counter control or control standard	Multi-energy source covering the general energy calibration range	Control limits: three sigma or ∀ 3%, whichever is greater[b] System attributes such as count rate, energy calibration, and/or energy resolution (FWHM) for control peaks should be monitored.	Readjust if kev/channel drift occurs Investigate. Recalibrate if necessary.	One per week or after analytical run whichever is longer

Notes:

FWHM = full width half maximum.

[a]See Section 4.4.1 for calibration standards requirements.

[b]Only where counting efficiency is an analytical requirement.

[c]The purpose is to confirm or establish current background and to test instrument contamination.

Table 4-3. Minimum Requirements of Calibration, Background, and Counter Control for Alpha Spectrometry.

Calibration Requirements	Calibration Parameters and Standards[a]	Criteria	Corrective Actions	Frequency
Calibration	Energy calibration	Use at least two alpha isotopes with resolvable energies[b]	Not applicable	After repair or major maintenance if control of system cannot be re-established
	Counting efficiency[b] Matrix- and geometry-specific	Use at least one recognized alpha source	Not applicable	
Background	Count detector background to establish background level	Represents the background for the time when the sample is counted[c]	As needed to meet data quality objectives	At a minimum of every 4 weeks or after analytical run which ever is longer
Counter control or control standard	At least two isotopes	Monitor peak location and resolution and efficiency (where counting efficiency is an analytical requirement). Control limits: three sigma or ∀ 3%, whichever is greater[b]	Readjust if kev/channel drift occurs Investigate. Recalibrate if necessary.	One per week or after analytical run whichever is longer

Notes:

[a]See Section 4.4.1 for calibration standards requirements.

[b]Only where counting efficiency is an analytical requirement. The counting efficiency for alpha spectrometers is independent of alpha energy. The counting efficiency need not be directly determined for a detector, if the analyte is determined relative to an appropriate recognized-traceable internal tracer. The alpha energy peak used for calibration shall be resolvable from other peaks in the spectrum or use a peak fitting correction if integration is affected by tailing. Equally acceptable, the counting efficiency may be determined for the system and factored into the sample activity determination as long as the basis for the efficiency determination remains constant with the samples, i.e., reproducible counting geometries. At a minimum, one recognized alpha source is used to determine the detector counting efficiency.

[c]The purpose is to confirm or establish current background and to test instrument contamination. At a minimum, the most recent background and its error obtained from the counting system should be used for background subtraction. More thorough means (e.g., 10-point running average background) for determining the appropriate background rate and its error may be appropriate for particular situations, and their uses shall be left to the discretion of the radiochemist.

Table 4-4. Minimum Requirements of Calibration, Background, and Counter Control for Beta Spectrometry.

Calibration Requirements	Calibration Parameters and Standards[a]	Criteria	Corrective Action	Frequency
Calibration	External (instrumental) standardization	Not applicable	Not applicable	After repair or major maintenance, if system control cannot be re-established
Method calibration (determining quench)	1. Quench curve[b] at least three points for applicable quench range bracketing the sample quench characteristic 2. Internal standard	Used for establishing quench level in the sample and to determine specific counting efficiency	Investigate the system	1. If matrix or cocktail changes 2. Add to each sample type
Counter control background	Count system background	Used to examine instrumental contamination. Not used for sample background subtraction	Investigate the system	One per day when the system is used
Blank	Use similar matrix of the sample Use for calculation	Used to determine matrix-specific background count rate as sample background subtraction	Investigate the system	One per day when the system is used

Table 4-4. Minimum Requirements of Calibration, Background, and Counter Control for Beta Spectrometry.

Calibration	Calibration Parameters	Criteria	Corrective	Frequency

Requirements	and Standards[a]		Action	
Counter control or control standard	Analyte specific if applicable reliable source, e.g., vendor-supplied sources)	Control limits: Three sigma or ± 3%, whichever is greater	Investigate	One per day when the system is used
Alternate calibration: batch approach[c]	Minimum two matrix-matched standards and blanks	Counting efficiency control limits: three sigma ± 5%, whichever is greater	Investigate	Count blank and standard at beginning and end of run based on matrix type

Notes:

[a]See Section 4.4.1 for calibration standard requirements.

[b]If applicable.

[c]This is an alternate calibration. If this approach is used, the above requirements do not apply

4.4.2 Inorganic Analysis

Instrument calibration should be performed based on manufacturer's recommendations and should establish a working response range. Calibration requirements such as frequency, criteria, and corrective action for inorganic analysis are provided in Table 4-5. Accuracy of the calibration shall be confirmed by performing an initial calibration verification immediately after calibration (see Section 6.5.2). The performance of an instrument measurement system during an analytical run shall be verified by a

continuing calibration verification (see Section 6.5.3).

The laboratory is required to take corrective action when measurement systems fail calibration QC criteria as demonstrated by the procedures discussed in Section 5.0.

Table 4-5. Minimum Calibration Requirements for Inorganic Analyses.

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
Inductively coupled plasma spectrometer (ICP)	Profile (optical alignment).	Before each new analytical run[a].	Meet manufacturer's recommendations for centroid and full width half max.	Investigate. Correct if necessary.
	Blank and one concentration per analyte of interest.		Confirm acceptability using initial calibration verification[b].	Investigate. Correct. Recalibrate as required.
ICP/mass spectrometer (MS)	Tune.	Analyze four times at the beginning of each analytical run.	RSD ≤ 5%.	Investigate. Correct.
	Check mass calibration		Mass calibration must be less than 0.1 amu of actual value. Resolution must be less than 0.9 amu full width at 10% peak height.	Adjust mass calibration to correct value.
	Calibrate using at least a blank and one standard according to manufacturer's recommendations.	Before each analytical sequence.	Calibration verification within ± 10% of true value.	Investigate. Correct. Recalibrate.
Graphite furnace atomic absorption (AA) and flame AA]	Blank and three concentrations that bracket instrument working range.	Before each new analytical run[a].	Meet coefficient correlation of >0.995. Confirm acceptability using initial	Investigate. Correct. Recalibrate as Required.

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
			calibration verification[b].	
Hydride AA (arsenic and selenium)	Blank and five standards.	Before each new analytical run[a]	Meet coefficient correlation of >0.995. Confirm acceptability using initial calibration verification[b].	Investigate. Correct. Recalibrate as required.
Cold vapor (manual atomic absorption)	Blank and three concentrations that bracket 5 μg/L working range or blank and four concentrations that bracket 10 μg/L working range.	Before each new analytical run[a].	Meet coefficient correlation of >0.995. Confirm acceptability using initial calibration verification[b].	Investigate. Correct. Recalibrate as required.
Automated	Blank and 4 standards (linear response). Blank and 8 standards (non-linear response).	Before each new analytical run[a].	Meet coefficient correlation of >0.995. Confirm acceptability using initial calibration verification[b].	Investigate. Correct. Recalibrate as required.
Cyanide-manual and semiautomated spectrophotometric[c]	Blank and three concentrations (undistilled) that bracket working range.	Before each new analytical run[a].	Meet coefficient correlation of >0.995. Confirm acceptability using initial calibration verification[b]. The distilled standard require-	Investigate. Correct. Recalibrate.

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
			ment is covered by the Laboratory Control Sample LCS, Table 6-3.	
Ion chromato-graphy	Blank and three concentrations that define working range.	When calibration verification fails.	Meet coefficient of correlation >0.995. Confirm acceptabil-ity using initial calibration verifica-tion[b].	Investigate. Correct. Recalibrate as required.
pH	Two point, calibration; 3 pH units or more apart calibration range representative of sample results. For corrosivity characterization, one buffer should be a pH of 2 for acidic wastes and pH of 12 for caustic wastes.	Before each new analytical run[a].	For dial or slope calibration, analysis of calibration standards must measure within 0.05 pH units of true value A calibration verification standard within 0.1 pH units of true value confirms acceptability of calibration	Investigate. Correct. Recalibrate as required.
Ion selective electrode Working curve technique	Minimum of three standards with one near the estimated quantitation limit (EQL), to define the working range.	Before each new analytical run[a]. All samples.	Calibration verifica-tion within ± 10% of true value.	Investigate. Correct. Recalibrate as required.

Instrument or Test	Calibration Criteria	Frequency	Acceptance Criteria	Corrective Action
Known-addition, double known-addition or standard-subtraction technique	Follow manufacturer's method-specific recommendations.	standards and blanks.	Calibration verification within ∀ 3 standard deviation of the historical mean.	
Titrimetric	N/A	N/A	Standardize titrant(s) before use. Evaluate results based upon QC presented in Section 6.5.2 and 6.5.3.	N/A
Colorimetric	Blank and minimum of three standards, with one near the EQL, to define the working range.	Before each new analytical run[a].	Calibration verification within ± 10% of true value.	Investigate. Correct. Recalibrate as required.

Notes:

[a]Analytical run is defined as sequence of analyses within a continuous time period. See Section 6.5.1.

[b]See Section 6.5.2 for initial calibration verification acceptance criteria.

[c]For dedicated cyanide spectrophotometers/colorimeters, a blank and six standards shall be run. This calibration shall remain valid as long as calibration verification acceptability is demonstrated or for up to 90 days.

N/A = not applicable.

4.4.3 Organic Analysis

Instrument calibration shall be performed to establish a working response range. Calibration requirements for frequency, criteria and corrective action for organic analysis are provided in Tables 4-6, 4-7, and 4-8. The calibration accuracy shall be confirmed by performing an initial calibration verification immediately after calibration (see Section 6.7.2). The performance of an instrument measurement system during an analytical sequence shall be verified by a continuing calibration verification (see Section 6.7.3).

The manufacturer's specifications for tuning the gas chromatograph/mass spectrometer (GC/MS) system shall be met before calibration. All systems incorporating a GC should have the retention time window specifications evaluated each time the GC system parameters are changed and whenever a new column is installed.

Continuing calibration should be verified routinely or before running samples. The laboratory is required to take corrective action when organic measurement systems fail calibration as demonstrated by the procedures discussed in Section 5.0.

Table 4-6. Minimum Requirements for Gas Chromatograph/Mass Spectrometer System.

Calibration	Calibration standards	Acceptance Criteria	Corrective Action	Frequency
Tuning instrument performance check	Specific tuning compound, either purge or inject	Shall meet regulatory criteria if applicable, otherwise meet manufacturer's recommendation.	Re-tune or repair as necessary	12 hours
Calibration (initial)	Numbers of concentrations of analytes of interest are based on RCRA, CERCLA, or others[c] See CCV All compounds used are required by laboratory and client agreement	Validate calibration curve to meet appropriate regulatory or others[c] criteria for response factor and % relative standard deviation	Not applicable	Upon failure of initial calibration verification
System performance check compounds (SPCC)[b] when appropriate	Compounds used are based on RCRA, or others[c]	Meet appropriate regulatory or others[c] criteria	Investigate the system or re-run	Run with every initial calibration and CCV
Calibration check compounds (CCCs)[b] when appropriate	Compounds used are based on RCRA, or others[c]	Meet appropriate regulatory or others[c] criteria	Investigate the system or re-run	Run with every calibration and CCV to ensure calibration and CCV is within control
Continuing calibration verification (CCV)	Mid-range calibration standard and internal standards All compounds	Validate calibration curve to meet regulatory or others[c] criteria for response factor, retention time and % difference	Investigate the system and initiate corrective action	12 hours

Calibration	Calibration standards	Acceptance Criteria	Corrective Action	Frequency
	used are required by laboratory and client agreement	between initial and continuing calibration		
Internal standards[d]	Compounds used are based on RCRA or CERCLA	Meet appropriate regulatory criteria	Investigate the system or re-run CCC, and re-run any sample with internal standard not meeting criteria	Included in every standard solution, blank, and sample
Surrogates	Similar behavior to analyte of interest When performing an established method, all requirements shall be followed, unless client requests otherwise	Meet appropriate regulatory or other criteria[c]	Not applicable	Included in every sample, calibration, and CCV

Instrument/ Method blank	Analyte free water, surrogates, and internal standard	All analytes less than detection limits with the exceptions based on RCRA, CERCLA, or others[b]	Correct problem. Re-run any samples that are affected.	Run one blank before sample analysis.

Notes:

CERCLA = *Comprehensive Environmental Response, Compensation, and Liability Act*
RCRA = *Resource Conservation and Recovery Act*

[a]RF is equivalent to RRF for Contract Laboratory Program.

[b]Nomenclature is based on SW-846.

[c]Other criteria that are required by either a data quality objective, laboratory and client agreements, or regulator approval.

[d]Internal standard shall be used. Internal standard specific compounds are suggested and not mandatory. If other compounds are chosen, they shall cover the entire retention time range, not interfere with analytes, and not degrade. The primary ion from the appropriate internal standard compound is used to ratio to the ion from the analyte of interest.

Table 4-7. Minimum Requirements of Calibration and Calibration Verification for Gas Chromatograph System.

Calibration Requirements	Compounds	Criteria	Corrective Actions	Frequency
Calibration: External standard approach	Minimum three concentrations per analyte of interest with one near the method detection limit to define the working range of the detector[a] Target compounds[b] or analytes per laboratory and client agreement Surrogates	Calibration factor (CF) and %relative standard deviation (RSD) shall be calculated for each compound Validate the calibration curve to meet regulatory or others[c] criteria for % RSD of CF	Investigate the system or re-run if necessary	After major maintenance or upon failure of continuing calibration verification
Alternate calibration: Internal standard approach	Minimum three concentrations per analyte of interest with one near the method detection limit to define the working range of the detector[a] Target compounds[b] or analytes per laboratory and client agreement Surrogates Add internal standard to all standards and samples.	RF and %RSD shall be calculated for each compound If an RF value is constant over the working range, validate the calibration curve and use it for calculations	Investigate the system or re-run if necessary	After major maintenance or failure of continuing calibration verification
Continuing calibration verification	Using one or more calibration standards	Working calibration curve verified by the measurements of one or more calibration standards	Investigate the system or re-run a new calibration	Daily, when used, and before analytical run

Calibration Requirements	Compounds	Criteria	Corrective Actions	Frequency
		Meet % difference of CF criteria between initial and continuing calibration based on RCRA, CERCLA, or others[c]	curve	

Notes:

CERCLA	=	Comprehensive Environmental Response, Compensation, and Liability Act
RCRA	=	Resource Conservation and Recovery Act
RF	=	response factor
RSD	=	relative standard deviation

[a]For RCRA or CERCLA type of work, either SW-846 or Contract Laboratory Protocol shall be used.

[b]Select one or more internal standards similar in analytical behavior to the compounds of interest.

[c]Other criteria are required by either a data quality objective, laboratory and client agreements, or regulator approval.

Table 4-8. Minimum Calibration Requirements for Total Organic Carbon, Total Inorganic Carbon, and Total Carbon Analysis Using Different Instruments.

Instruments	Calibration	Frequency	Acceptance Criteria	Corrective Action
Combustion-infrared method. Persulfate-ultraviolet oxidation. Wet-oxidation method	According to manufacturers recommendation Blank and sufficient standards should be used that encompasses the expected concentration	Before each new analytical run[a] or every 15 samples	Follow manufacturer's recommendations	Investigate. Correct if necessary. Recalibrate as required.
Coulometric method	Initial calibration performed by manufacturer	Confirm acceptability using performance check	± 3 standard deviation of historical mean of the performance check	Investigate. Correct if necessary.

4.4.4 Physical Testing

Minimum calibration requirements for several physical tests are presented in Table 4-9.

Table 4-9. Minimum Calibration Requirements for Thermogravimetric Analysis, Differential Thermal Analysis/Thermal Gravimetry, and Differential Scanning Calorimetry.

Technique	Calibration Requirements	Criteria	Frequency	Corrective Action
Thermogravimetric analysis	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and balance checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established
Differential thermal analysis/thermal gravimetry	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and balance checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established
Differential scanning calorimetry	Initial calibration performed by manufacturer	Confirm acceptability using performance check (temperature and enthalpy checks)	Upon failure of performance check	Recalibrate when performance cannot be re-established

5.0 DATA COLLECTION, REDUCTION, AND REPORTING

Data collecting and reporting processes include proper sampling, correct chain-of-custody, collection of raw data, data reduction and calculations, and transferring results to a final form for reporting. All of these records shall be maintained in a manner to safeguard the data and meet regulatory requirements as described in Volume 1, Section 6.0.

5.1 DATA COLLECTION

Raw data are all parameters used to calculate a final reportable result. Raw data can be generated by manual and/or electronic means. Manual data generation shall be collected and recorded by the analyst according to applicable procedures. Many analytical instruments are interfaced with computers and/or integrators and are able to generate or reduce the raw data into reportable results.

Entries into logbooks shall be made in a manner such that they can be easily read, understood, and reproducible with standard photocopier.

Raw data output shall be retained as a part of the records (see Volume 1, Section 6.0). Information on date of sample collection, sample preparation, and analysis run; sample identification numbers; analyst or instrument operator; type of analysis; and procedure number, including revision number, shall be traceable to the raw data output.

5.2 DATA REDUCTION

Data reduction is defined as the mathematical operations applied to the raw data to produce a final reportable result. Data resulting from analyzing samples shall be reduced according to applicable procedures. Data reduction includes activities that convert instrument and computer responses into reportable results. These activities may involve calculations, changes to the units or the data values, and statistical and mathematical analysis.

Computer programs or spreadsheets used for data reduction shall be verified before reporting data to ensure calculational and data manipulation programs perform properly.

The following practices shall be in place to ensure accuracy of data entry, proper calculation, and appropriate data reduction:

Verify that all readings or output are accurate.

Ensure proper error correction or data change, i.e., one line through, dated, initialed,

and explained as appropriate.

Select appropriate formulas for calculating final results, correct for appropriate backgrounds and/or interference (e.g., compton effects for GEA and inter-element correction for inductively coupled plasma spectrometer [ICP]), and document calculations and results.

Verify that data are accurately transcribed into notebooks, forms/benchsheets, or spreadsheets.

5.2.1 Significant Figures

Significant figures reflect the limits of the particular analysis method. Basic rules for significant figures and for calculating values and retaining the number of significant figures are provided in *Standard Practice for Using Significant Digits in Test Data to Determine Conformance with Specifications*, ASTM E-29 (ASTM 1993a). Reported values should contain only significant figures.

Recognizing that vendor-supplied software may not meet the general rules for significant figures, the laboratory should work with the client to determine the best way to report results, based on the project needs.

5.2.2 Rounding-Off Methods

When a figure is to be rounded to fewer digits than the total number available, the rounding-off procedure described in ASTM E-29 (ASTM 1993a) should be followed. If a different rounding method is used it shall be noted in the narrative. A brief description of the procedure follows.

When the first digit discarded is less than 5, the last digit retained should not be changed.

When the first digit discarded is greater than 5, the last figure retained should be increased by 1.

When the first digit discarded is exactly 5, followed only by zeros, the last digit retained should be rounded upward if it is an odd number, but no adjustment made if it is an even number.

5.2.3 Data Review

Data review refers to the process of determining whether data conform to specified requirements. A system shall be in place in accordance with laboratory-established procedures to review data before

data reports are issued. Errors detected in the review process shall be referred to the analyst for corrective action (see Volume 1, Section 5.0). The data review process shall incorporate the following elements and those discussed in Section 8.0.

Data shall be reviewed according to laboratory procedures to verify that calculations are correct and to detect transcription errors.

Sample data review shall include verification of sample identification number, analyst, and date of analysis.

Data shall be reviewed against applicable QC and method criteria to verify that the preparative and/or analytical system is performing acceptably (see Section 5.0 for details). If QC samples did not meet QC criteria, data within the batch shall be evaluated to determine if there were any adverse effects on the data; the sample shall be re-prepared and/or re-run or the data shall be reported with qualification(s), which will be detailed in the narrative as appropriate to the condition.

Random checks shall be performed to verify data entry, calculations, and QC criteria.

5.3 DATA REPORTING

The analytical information reported should include the measured parameters, the details of analysis, and the reported data values in accordance with client requirements.

Inorganic or organic results shall be reported as numeric values with appropriate data qualifiers if above the instrument detection limit (IDL) (see Section 7.5.1.2 for details). If the value is less than IDL, it can be reported as undetectable.

Radiochemical results shall be reported based on calculated concentration or activity values (whether negative, positive, or zero) using the appropriate blank for each nuclide (see Section 7.5.2 for details). The measured activity or concentration should be reported with estimates of total propagated uncertainty but without comparison to the estimated *a priori* minimum detectable concentration (MDC). The MDC should not be reported to the client *in lieu* of low-level measurements.

5.3.1 Data Reporting Documentation

The reporting documentation shall include the following information:

Laboratory name and address.

Sample information including unique laboratory identifier cross-referenced to client identification, sample collection date and time (when holding times apply or upon request), date of sample receipt, and date(s) of sample preparation and analysis.

Identify results obtained from subcontracted laboratories

Analytical units and results, reported with an appropriate number of significant figures, and associated uncertainty.

Detection limits.

Method references.

Identification of any amended test results.

Signature and title of person accepting responsibility for the report contents.

Date of issue.

Identification of subcontracted results if applicable.

Appropriate QC results (correlation with sample batch shall be traceable and documented).

Appropriate data qualifiers with definitions and a narrative on the quality of the results if applicable.

Additional data reporting, (i.e., the percent of moisture/solid or correction for equivalent dry weight) as appropriate.

5.3.2 Immediate Reporting

An immediate data reporting system shall be established between the laboratory and the client to address an emergency situation. The type of information, level of approval, data reporting format, and means of delivery shall be discussed and agreed upon between the laboratory and the client. The emergency situation may include but is not limited to screening activities for safety issues, critical analytes, or limiting sample amount.

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6.0 QUALITY CONTROL

QC is defined as the overall system of activities that provides checks and balances to the quality of a product or service. QC data are evaluated against client requirements to measure how well the data meets the client's needs. The goal is to provide data of known quality that is adequate for the intended purpose. QC data allow the laboratory and the client to measure the degree of conformance against the requirements.

To assess the precision, accuracy, and sensitivity of a reported result, QC checks are incorporated throughout the data collection process (e.g., sample preparation/separation, analysis, reporting) to provide a measurement tool for evaluating the effectiveness of the process. QC checks provide information with regard to performance of the measurement system and environmental as well as matrix-related impacts on the measurement system. The information gained from evaluating QC performance can then be used to implement corrective actions or improve processes.

The quality control requirements for each of the three major types of analysis conducted in support of Hanford environmental programs, radiochemical, inorganic and organic are discussed separately. Physical testing quality control requirements are also provided for several test parameters (Section 6.8). Each of the fields of chemistry is further sub-divided into two parts, preparation/separation QC and measurement/counting QC. The text and the accompanying tables provide the detailed QC requirements for each topic. Basic QC operations, applicable to all analytical disciplines, are presented in Section 6.1. Basic QC operations consist of controlling the quality of solvents, standards, reagents, and gases used in the laboratory.

The QC requirements presented are designed to enable both the laboratory and the client to ascertain the quality of the data produced. These QC checks provide information on the precision, accuracy, sensitivity, and overall reliability of the reported results. Each laboratory is required to implement and meet the QC requirements outlined in this section. However, client data quality requirements shall always be used to determine whether sample results can be reported. In certain instances, a result may fall outside of the specifications in this chapter but still meet client needs. In such cases, the results would be considered acceptable for reporting. Reported results shall be traceable to the QC performed with those results.

6.1 GENERAL LABORATORY QUALITY CONTROL

The QC described in this section represents the basic laboratory systems associated with analytical operations and applies to radiochemical, inorganic and organic analytical procedures. The use of substandard reagents, standards, materials, and equipment can result in less reliable or unreliable data. Each laboratory shall have a mechanism in place for demonstrating control over those sources which affect the accuracy, precision, and sensitivity of reported results. The minimum requirement would consist of monitoring analytical and preparative blanks for contamination from these sources.

6.1.1 Distilled or Deionized Water

High-purity water is generally defined as water that has been distilled or deionized, or both, so that it will have a conductivity less than 1.0 μmho/cm (greater than 1.0 megaohm-cm resistivity). Each laboratory is responsible for ensuring that the water used for data collection activities is of sufficient quality for the operation performed. Water quality is regularly monitored via preparative and analytical blank performance.

6.1.2 Compressed Gases

Each laboratory shall monitor the quality of gases used in the laboratory to ensure that they are adequate for the operation being performed. At a minimum, this shall consist of monitoring system performance (e.g., for contribution to background and/or blanks from impurities).

6.1.3 Standards

The acceptability of standards used in the preparation and analysis of client samples shall be verified. Each laboratory shall document its method(s) of verification. See Section 4.3 for guidance on standard selection, use, and verification.

6.1.4 Reagents

Each laboratory is responsible for ensuring that reagents used for data collection activities are of sufficient quality for the operation performed. Reagent quality is regularly monitored via preparative and analytical QC performance.

6.1.5 Labware

Each laboratory shall purchase and use labware of sufficient quality to meet client requirements. Labware selected shall be compatible with the testing performed.

6.1.6 Glassware Cleaning

Glassware cleaning shall be performed in a manner that minimizes sample contamination.

6.1.7 Good Housekeeping

Each laboratory shall maintain their operations in a clean and organized manner to maximize available workspace and minimize environmental impacts on samples.

6.2 PREPARATIVE TECHNIQUES FOR RADIOCHEMISTRY

Preparative techniques are those operations used to prepare a sample for instrumental analysis (i.e., counting). Radiochemistry generally separates preparative techniques into two types, sample preparation which prepares the sample material for the second step, radionuclide separation (isolation). The first step, sample preparation, modifies the original sample matrix freeing the radionuclides for further separation prior to counting (quantitation). Examples of preparative techniques are evaporating water samples to dryness, acid leaching soils and air filters, wet ashing organic matter, fusion, and acid digestion. Separation involves isolating specific radionuclides from other radionuclides that may interfere with accurate quantitation of the target analyte. Examples of separation techniques include ion exchange chromatography and selective solvent extraction.

In this context, separation and/or isolation techniques are preparative if performed before counting to facilitate accurate measurement. Simple dilution is not a sample preparation technique. Selection of preparative technique should be based on client data quality requirements. See the discussion below and Table 6-1 for frequency requirements used during preparation.

6.2.1 Preparation/Separation Batch

A batch is a group of samples, of similar matrix type, prepared and/or separated at the same time. A batch shall not exceed 20 client samples. If clients do not specify project-specific QC, the laboratory may combine up to 20 samples of similar matrix type for preparation with only one duplicate (or matrix spike duplicate) and matrix spike required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or matrix spike duplicate) and matrix spike may be performed for every 20 client-specific samples received. However, the preparation blank and laboratory control sample/blank spike requirement would apply to each batch of samples prepared at one time.

A sample or series of samples which do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and matrix spike requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed upon by the laboratory and the client before work begins.

6.2.2 Preparation Blank or Method Blank

The sample preparation blank or method blank is used to monitor contamination resulting from the sample preparation process. The preparation blank or method blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed (i.e., clean soil, synthetic tank waste) provided the matrix is free of contamination from analytes of interest above those naturally occurring in nature.

The weight or volume of blank material used should be selected such that it will result in a reasonable approximation to that of the samples and shall be presented in the same context as the samples. In any event, the blank should be evaluated for it contribution to the sample, based upon how the sample was prepared. Preparation or method blanks shall be prepared with each batch of samples processed at the same time.

Preparation or method blank acceptability shall be demonstrated as follows: 1) the blank shall be less than the estimated MDC of the associated samples, or, if the blank is equal to or above the estimated MDC, 2) it shall not exceed 5% of the measured activity present in the associated samples, or, when a decision level is specified, 3) the blank shall not exceed 5% of the decision level unless 2) above applies. Note: The laboratory must be capable of achieving an MDC less than or equal to 5% of the Decision Level or must negotiate an acceptable alternative.

All affected samples in the preparation batch will be re-prepared and re-analyzed if the preparation blank (method blank) fails to meet one of the acceptance criteria unless client specific data quality requirements dictate otherwise. The client shall be notified prior to such actions when additional costs will be incurred.

The results of the preparation blank analysis should be reported to the client as part of routine reports. Preparation blank results are not subtracted from sample results unless client data quality requirements specify otherwise; in which case, the case narrative accompanying the results should state that blank subtraction was used.

Table 6-1. Preparative Requirements for Radiochemistry Quality Control.

Quality Control Requirements	Frequency	Criteria	Corrective Action
Preparation/ method blank[a]	1 per batch	<MDC, <5% Sample isotope concentration, or <5% decision level.	Evaluate use against analyte level present in samples and client DQRs. Reprepare and analyze affected samples.
Blank spike[b] -or- Laboratory control sample	1 per batch ---------- 1 per batch	80% to 120% or statistical[c] ---------- Vendor or statistical[c]	Investigate, Evaluate against DQRs, Correct, Reprepare and analyze as applicable.
Sample Duplicate[a]	1 per batch	≤20% relative percent difference when results have and individual uncertainties (1 sigma) ≤15%[d].	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Matrix or Post spike[b]	1 per batch	75% to 125% or statistical[c]	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.

Notes:

DQRs = data quality requirements.

[1]Nondestructive radioanalytical techniques do not require a matrix spike; however, a blank spike or laboratory control sample is desirable.

[2]Refer to Tables 4-1 through 4-4 for counter control and background frequencies.

[3]Shall be applied at original preparation stage.

[4]The decision to perform a spike during or after preliminary preparation shall be based on sample activity levels. This spike requirement may be met using a matrix spike, tracer, or carrier depending on client requirements and considerations discussed in this Section.

[5]Lab developed procedures shall either meet specifications or show statistical basis for

alternative criteria. Alternative criteria is acceptable if it meets client DQRs.

[6]This represents the 68% confidence level

6.2.3 Laboratory Control Sample or Blank Spike

A laboratory control sample (LCS) or blank spike (BS) is used to monitor the effectiveness of the sample preparation process. The laboratory control sample is a material similar in nature to the sample being processed containing the isotope(s) of interest (e.g., standard reference material). A laboratory control sample, if available, shall be prepared with each batch of samples processed at the same time. The blank spike is distilled or deionized water or other suitable substrate spiked with the isotope(s) of interest. The blank, spiked with tracer would also meet the BS requirements. A blank spike is normally used when an appropriate laboratory control sample is unavailable.

Blank spike control is demonstrated by target analytes being within either the preset limit of 80%-120% or, within statistically determined limits when the ∀20% criteria cannot be reliably achieved.

Laboratory control sample acceptability is demonstrated by target analytes being within established control or tolerance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor supplied precision may effect the tolerance limits applied to the analyte.

The laboratory must ensure that each method used for a given scope of work is capable of meeting client precision and accuracy requirements or the lab must negotiate alternative requirements.

All samples in the preparation batch shall be re-prepared and analyzed for those analytes in which the acceptance criteria for the LCS or BS has not been met. In limited cases, results may be acceptable for reporting provided the lab can demonstrate that the client DQR was still achieved. The client shall be notified prior to repreparation if additional costs will be incurred.

The laboratory control sample/blank spike results should be reported to the client. No adjustment of client sample results based on LCS recovery is made in the laboratory report.

6.2.4 Matrix or Post Spike

In general, matrix spike is a term given to a client sample which has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The matrix spike is used to monitor method performance in a specific sample matrix. Matrix spike results are an indicator of the effect the client sample matrix has on the accuracy of measurement of the target analytes.

In radiochemistry, the matrix spike represents the addition of a known quantity of the isotope of interest to an aliquot of sample. This spike may be added to a sample aliquot prior to any sample preparation i.e., fusion, leaching. Alternatively, it may be elected prior to specific radiochemical manipulation e.g., separation chemistry or evaporation onto a planchet. A spike added at this point can indicate matrix related effects remaining after preparation but gives no measure of the efficiency of the original

preparation step. Whenever practical, other spike recovery data (i.e., inorganic recovery results from the same preparation should be used to identify potential analyte losses).

The decision on when and how to spike a sample is based on the anticipated sample analyte activity or required dilution. Spiking additional activity into a sample that already exhibits high activity is not justifiable, either because of standard material consumption or radiation dosimetry issues. Likewise, spiking before a large dilution can waste expensive standard material. Therefore, spiking may be performed after preliminary sample preparation and dilution, but before any radiochemical separation occurs. However, spike amounts should always provide results exceeding the decision or action limit.

Each laboratory shall evaluate matrix spike recovery information against client data quality requirements. The goal is to ensure that limitations on the data, caused by the sample matrix and represented by matrix spike performance, are adequately portrayed and discussed in the report to the client. It should be noted that client results would already be corrected for matrix and/or handling effects if a tracer or carrier is used in place of a matrix spike.

When the analyte concentration is unknown, spiking is typically performed at a level that is one of the following: 1) equivalent to the threshold established by the DQO process 2) specified by method, or 3) 1 to 5 times the minimum detectable activity. Otherwise, (as general guidance) the spiking should be performed at a level equivalent to 1 to 5 times that of the sample. In those instances where the analyte concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the analyte response of the spiked sample is statistically significant. If not, a re-run of the process may be required depending on client needs. For radiochemical analysis, matrix spike control is demonstrated when target analytes are within established control limits. Control limits are established by one of the following: 1) established by the DQO or DQR process for a particular project or program, or 2) laboratory performance over time in samples of similar matrix and concentration levels.

A matrix spike shall be prepared with each batch of 20 samples and the results reported to the client along with the calculated recovery (see Section 7.3.1). No adjustment of the client sample results is made in the laboratory report.

Note: Situations may exist where there is no spike material available, e.g., ^{93}Zr. In such cases, method performance must rely on tracers and/or carriers.

6.2.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory duplicates are two aliquots of the same sample (intralaboratory splits) that are taken through the entire sample preparation and analytical process. Spike duplicates are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. Duplicates are

used to assess the precision of the preparation and counting process in a client-specific matrix. The degree of agreement between duplicates indicates the reproducibility (precision) of the combined preparation/separation, and measurement process.

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process (e.g. isolated particles of plutonium in a soil matrix which cannot be reliably sampled using standard laboratory sub-sampling techniques). Disagreement may arise if the method has poor applicability to the analyte/matrix system.

Typically, radiochemical preparations include a sample and sample duplicate. In cases where the sample is not expected to contain concentrations of target analytes sufficient to produce relatively small counting errors, the use of a matrix spike and matrix spike duplicate should be considered.

Radiochemical laboratory duplicate RPD criteria is set at 20%. This criteria shall only be applied to an analyte concentration or activity which has an uncertainty (1 sigma) less than or equal to 15%. When either the sample or duplicate uncertainty exceeds 15% the data shall be evaluated based on statistical comparability. The laboratory can also perform an evaluation using the mean difference. The mean difference calculation takes the uncertainty of each individual measurement into account when comparing the two results. The formula for calculating the mean difference is presented in Section 6.0.

In those cases where the criteria above are not met evaluation of the source of error and impact on client DQRs shall be performed. When client DQRs can not be met the client shall be notified; results shall either be accepted or new work scope (methodology) agreed upon.

6.2.6 Tracer

Radiochemical techniques typically employ either a tracer, carrier, or matrix spike, or a combination of a matrix spike with a tracer or carrier. A tracer is used to correct radiochemical yield in a specific sample. The amount of tracer recovered through a method reflects effectiveness of the radiochemical separation for the target analyte. Criteria for selection and recovery of tracers shall be specified.

The tracer may be added to an aliquot of prepared (e.g., leached), or diluted sample prior to specific radiochemical manipulations (e.g., separations). The tracer added at this point can indicate matrix-related effects remaining after preparation but gives no measure of the efficiency of the original preparation step. Isotopic exchange with the analyte is assumed. The decision on when to spike a sample with tracer is based on the expected analyte activity in the sample. Whenever practical, other spike recovery data (i.e., inorganic recovery results from the same preparation) should be used to identify potential analyte losses.

For most radiochemical applications, a tracer is considered radioactive and massless. As such, it can be added to all samples in an analytical batch as a sample-by-sample QC measure (yield). The recovery of the tracer is used to correct for all losses of the target analyte. Sufficient tracer must be used to maintain counting statistics to support client DQO needs.

Note: High yields with radiochemical tracers are not always of great importance, provided that the yields can be evaluated (e.g., it is common to sacrifice yield to achieve a better separation). Before applying a yield correction, evaluation of whether or not sufficient counting statistics were achieved to make yield correction meaningful shall be made.

6.2.7 Carrier

For this discussion, a carrier is used to correct radiochemical yield in a specific sample. As with a tracer, the carrier recovery is a measure of the amount of analyte lost in performing the procedure. Criteria for selection and recovery of carriers shall be specified as use may be considered unique to the specific isotope being determined. The influence of a carrier on counting of the target analyte (e.g., mass attenuation of beta counting) must be addressed during procedure qualification. This affect may be considered as negligible, in cases such as in gamma counting.

The carrier may be added to an aliquot of prepared (e.g., leached) sample prior to specific radiochemical manipulations (e.g., separations). The carrier added at this point can indicate matrix-related effects remaining after preparation but gives no measure of the efficiency of the original preparation step. The decision on when to spike a sample with carrier is based on the expected analyte activity in the sample.

Note: High yields in radiochemistry are not always of great importance, provided that the yields can be evaluated (i.e., it is common to sacrifice yield to achieve a better separation). Before applying a yield correction, evaluations of whether or not sufficient measurable mass was achieved to make yield correction meaningful shall be made.

6.3 RADIOANALYTICAL TECHNIQUES

Analytical techniques are those operations which permit the measurement of a parameter of interest. For the purposes of this document, radiochemical analysis is the measurement of some property (α, β^-, or photon emissions) for which there is an instrument response that can be related to the concentration or amount of the radionuclide of interest in a sample or in some material prepared from the sample. Selection of analytical techniques should be based upon client data quality requirements. The QC requirements presented below are designed to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process.

6.3.1 Counting Sequence

An analytical sequence or run is defined as those samples counted on any specific detector in a period of time between counter control counts. Thus, by definition, the analytical run starts after the counter control source is counted and ends when the following counter control source is counted.

As a matter of good technique, the sequence of samples counted on a detector where the detector face is directly exposed to the sample should be traceable. Gas-flow proportional counters (alpha/beta counting)and silicon-barrier counters (alpha spectrometry) are examples of detector systems where the detector is exposed to the sample and contamination may occur. The sequence reconstruction will allow the analyst to better evaluate problems associated with data that may have been generated on a counter that was contaminated during the course of an analytical sequence.

6.3.2 Verification of Calibration

The calibration verification confirms the acceptability of the calibration. The calibration verification demonstrates that both the standards used and the calibration are accurate. Calibration verification shall be performed before commencement of sample analysis.

Calibration of counting instrumentation used in support of radiochemical measurements often applies over extended periods of time (e.g., years). Only one calibration verification needs to be performed after instrument calibration per geometry. Instrument stability, and thus calibration stability, is monitored by counter control standards (the equivalent of a continuing calibration verification, see Section 6.3.3).

The concept of calibration verification is accomplished in radiochemistry by using one of four methods: independent standards, use of independent measurements, multiple calibration curves, or data analysis. Examples of these concepts are provided below.

Use of independent standard

An independent standard (see Section 4.4) is prepared in the same geometry as the calibration standard. Standards prepared from a separate lot from the calibration standard are acceptable. The measured activity from the calibration verification standard shall fall within acceptable tolerance limits (as defined in the governing standard operating procedure).

Use of independent measurement

The calibration standard is measured on an independently calibrated detector for confirmation of the isotope activity(ies). This will confirm the standard was prepared correctly and will provide an accurate basis for the calibration.

Multiple calibration curves

Multiple calibration curves are often generated during instrument calibration(s) from multiple standard preparations (e.g., attenuation curves for multiple detectors, efficiency curves for multiple geometries). The data for these calibrations shall be evaluated for consistency.

Data analysis

Multiple radioisotopes are used to calibrate gamma spectrometers. The calibration curve generated shall be evaluated for smoothness of fit of the gamma energy to the counting efficiency. Gamma calibration curves shall be linear at higher energies (varies by detector and matrix) when plotted on a log-log scale.

6.3.3 Counter Control Standard (Continuing Calibration Verification)

In radiochemistry the counter control standard is used to monitor instrument stability over time. Acceptable performance demonstrates the continued accuracy of the calibration, indicating that the measurement system is still in control. The counter control standard may be prepared from any reliable source. Acceptable performance is demonstrated when the concentrations/activities measured fall within established control limits. See Tables 4-1 through 4-4 for counter control standard frequency and criteria.

Each analytical (counting) sequence shall be followed by an acceptable counter control during the next analytical sequence. Failure justifies corrective action and applies to all samples run since the last acceptable check. If no additional standard or spike information is present at the end of the preceding run, all data generated since the last acceptable counter control standard or QC sample shall be considered suspect and investigated.

The counter control standard verification should be performed very soon after the calibration is conducted. If prepared at a later date, it should be checked directly against the initial calibration standard to ensure consistency with time (this is especially important for a source which undergoes significant decay over its useful life).

The counter control standard should provide adequate counting statistics over the time period for which the source is to be counted. However, the source shall not be so radioactive as to cause 1) pulse pileups, 2) dead time that is significantly different from that to be expected from routine samples, or 3) gain shift in the case of pulse height analyzer systems.

6.3.4 Backgrounds

Radiochemical measurements typically include a background count. Background counts are a measure of system and/or environmental contributions and a fundamental aspect of the minimum detectable activity determination. Background count collection frequencies are listed in Tables 4-1 through 4-4. Background counts are normally subtracted from all subsequent sample counts and shall be recorded.

6.4 INORGANIC PREPARATIVE TECHNIQUES

Preparative techniques are those operations used to prepare a sample for analysis. Examples include: digestion, dissolution, extraction, phase partitioning, and/or leaching of a sample material. Separation and/or isolation techniques are also considered preparative if performed before analysis, to facilitate reliable analyte measurement. Simple dilution is not considered a sample preparation technique. Selection of preparative techniques should be based on client data quality requirements. See the discussion below and Table 6-2 for frequency requirements used during preparation.

6.4.1 Preparation Batch

A preparation batch is a group of samples, of similar matrix type, prepared at the same time. A batch shall not exceed 20 client samples. More than 20 samples can be prepared at the same time, if the required number of QC samples are performed for each batch. If clients do not specify project-specific QC, the laboratory may combine up to 20 samples of similar matrix type for preparation with only one duplicate (or matrix spike duplicate) and matrix spike required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or matrix spike duplicate) and matrix spike may be performed for every 20 client-specific samples received. However, the preparation blank and laboratory control sample/blank spike requirement would apply to each batch of samples.

A sample or series of samples which do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and matrix spike requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed upon by the laboratory and the client before work begins.

6.4.2 Preparation Blank (Method Blank)

The sample preparation blank (method blank) is used to monitor contamination resulting from the sample preparation process. The preparation blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed provided the matrix is free of contamination from analytes of interest (e.g., clean soil or sand for solid matrices). Interferences and/or unique ancillary contaminants produced by the blank matrix would be expected to be similar to that of the sample.

The preparation blank volume or weight shall be approximately equal to the sample weight or volume being processed and shall be presented in the same context as the samples. Preparation or method blanks shall be prepared with each batch of samples processed at the same time.
Preparation or method blank acceptability shall be demonstrated as follows: 1) the blank shall be less than the EQL of the associated samples, or, if the blank is equal to or above the EQL, 2) it shall not exceed 5% of the measured concentration present in the associated samples, or, when a decision level is specified, 3) the blank shall not exceed 5% of the decision level unless 2) above applies. Note: The laboratory must be capable of achieving an EQL less than or equal to 5% of the Decision Level or must negotiate an acceptable alternative. All affected samples in the preparation batch will be re-prepared and re-analyzed if the preparation blank (method blank) fails to meet the acceptance criteria.

All affected samples in the preparation batch will be re-prepared and re-analyzed if the preparation blank fails to meet one of the acceptance criteria unless client specific data quality requirements dictate otherwise. The client shall be notified prior to such actions when additional costs will be incurred.

The results of the preparation blank analysis and impacts on data shall be reported to the client as part of routine reports. Preparation blank results are not subtracted from sample results unless client data quality requirements specify otherwise in which case, the case narrative accompanying the results should state that blank subtraction was used.

Table 6-2. Preparative Requirements for Inorganic Quality Control.

Quality Control Requirements	Frequency	Criteria	Corrective Action
All Inorganic Techniques except pH			
Preparation blank or method blank[a]	1 per batch	<EQL, # 5% regulatory decision level, or # 5% of measured concentration in the sample	Investigate. Evaluate use against analyte level present in sample and client DQR. Reprepare and analyze for failed analytes.
Blank Spike -or- Laboratory control sample	1 per batch ---------- 1 per batch	80% to 120% or statistical[b] ---------- Vendor or statistical[b]	Investigate, Evaluate against client DQRs, Reprepare, and analyze for failed analytes as applicable.
Duplicate	1 per batch	# 20% RPD when result >EQL (10 times IDL)	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable and discuss in narrative.
Matrix spike	1 per batch	Recommended 75% to 125% or statistical	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQR, notify client if still unacceptable and discuss in narrative.
pH			
Duplicate	Every 10 samples	Not applicable	Discuss in narrative

Notes:

[a]Shall be applied to original preparation stage.

[b]Lab developed procedures shall either meet specifications or show statistical basis for alternative criteria. Alternative criteria is acceptable if it meets client DQRs.

EQL = estimated quantitation limit
IDL = instrument detection limit
RPD = relative percent difference.
DQR = data quality requirement

6.4.3 Laboratory Control Sample or Blank Spike

A laboratory control sample (LCS) or blank spike (BS) is used to monitor the effectiveness of the sample preparation process. The laboratory control sample is a material similar in nature to the sample being processed containing the analyte(s) of interest (e.g., standard reference material). A laboratory control sample, if available, shall be prepared with each batch of samples processed at the same time. The blank spike is distilled or deionized water or other suitable substrate spiked with the analytes(s) of interest. A blank spike is normally used when an appropriate laboratory control sample is unavailable.

Blank spike control is demonstrated by target analytes being within either the preset limit of 80%-120% or, within statistically determined limits when the ∀20% criteria cannot be reliably achieved.

Laboratory control sample acceptability is demonstrated by target analytes being within established control or tolerance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor supplied precision may effect the tolerance limits applied to the analyte.

The laboratory must ensure that each method used for a given scope of work is capable of meeting client precision and accuracy requirements or the lab must negotiate alternative requirements.

All samples in the preparation batch shall be re-prepared and analyzed for those analytes in which the acceptance criteria for the LCS or BS has not been met. In limited cases, results may be acceptable for reporting provided the lab can demonstrate that the client DQR was still achieved. The client shall be notified prior to repreparation if additional costs will be incurred.

The laboratory control sample/blank spike results should be reported to the client. No adjustment of client sample results based on LCS recovery is made in the laboratory report.

6.4.4 Matrix Spike

A matrix spike is a client sample that has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The matrix spike is used to monitor method performance in a specific sample matrix. Matrix spike results are a measure of the accuracy in the measurement of the analyte(s) of interest present in the client sample matrix.

When the sample concentration is unknown, spiking is typically performed at a level that is one of the following: 1) equivalent to the regulatory threshold, 2) specified by method, or 3) 1 to 5 times the EQL. Otherwise, the spiking should be performed at a level equivalent to 1 to 2 times that of the sample. When the concentration of the analyte in the original sample is greater than 0.1%, no matrix spike is required unless specified by client.

For inorganic analysis, matrix spike control is demonstrated when target analytes are within established control limits. Control limits are established by one of the following: 1) regulatory requirement, 2) the client via data quality requirements for a particular project or program, or 3) laboratory performance over time. The recommended criteria for most inorganic analysis is recovery within 75% to 125%.

If the matrix spike recovery fails to meet the criteria, the batch results shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix and represented by matrix spike performance, are adequately portrayed and discussed in the report to the client.

In those instances where the sample concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the recovery of the spiked sample is meaningful.

A matrix spike shall be prepared with each batch of 20 samples and the results reported to the client along with the calculated recovery. No adjustment of the client sample results is made in the laboratory report. Matrix spike performance shall be discussed in the report narrative.

In the case where a sample matrix cannot be spiked at the time of original preparation, then a post digestion spike shall be performed (Section 6.5.9). The term "matrix spike" can only be used when the sample is spiked at original preparation.

6.4.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory sample duplicates are two aliquots of the same sample (intralaboratory split) that are taken through the entire sample preparation and analytical process. Laboratory duplicates are used to assess the precision of the preparation and analysis process in a client-specific matrix.

Matrix spike duplicates are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. In cases where the sample is not expected to contain reasonable concentrations (analyte concentrations greater than ten times the instrument detection limit) of the analytes of interest, duplicate sample results will not provide a reliable estimate of precision. In these cases, matrix spike duplicates are used to demonstrate analytical precision in the client sample.

The degree of agreement between duplicates indicates reproducibility of the combined preparation/separation, and measurement process (precision).

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process (e.g. isolated particles of lead in a soil matrix which cannot be reliably sampled using standard laboratory sub-sampling techniques). Disagreement may arise if the method has poor applicability to the analyte/matrix

system.

One set of laboratory duplicates (or MS/MSD) is required for each batch of samples. Precision is estimated by calculating the relative percent difference (RPD) of the duplicate analysis (see Section 7.2.2). Upon receipt of instructions from the client, additional replicates can be performed. These additional samples will increase the likelihood of detecting non-uniformly distributed analytes in the client sample. It will also allow for a more accurate estimate of the variability of the overall analytical performance on client-specific samples/matrices. When more than two replicates are used, precision is expressed in terms of relative standard deviation (Section 7.2.1).

Typically, inorganic analyses include a sample and a sample duplicate because a high probability exists that the majority of those analyte(s) of interest will be detected in the sample. Inorganic duplicate RPD criteria is normally set at 20%; this criteria shall only be applied to analyte concentrations greater than 10 times the instrument detection limit (or method detection limit).

In those cases where the criteria above are not met, evaluation of the source of error and impact on client DQRs shall be performed. When client DQRs can not be met the client shall be notified; results shall either be accepted or new work scope (methodology) agreed upon.

Duplicate (or matrix spike duplicate) results shall be reported to the client along with the calculated RPD. Duplicate results shall be discussed in the report narrative.

6.5 INORGANIC ANALYTICAL TECHNIQUES

Analytical techniques are those operations which permit the measurement of a parameter of interest. Analysis is the measurement of some property for which there is an instrument response that can be related to the concentration or amount of the substance of interest in a sample or in some material prepared from the sample. Selection of analytical technique should be based upon client data quality requirements. The QC requirements presented below are designed to verify and document proper instrument operation and to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process.

6.5.1 Analytical Run or Sequence

An analytical run or sequence is defined as a group of samples analyzed together that may include one or more preparation batches. Each analytical sequence has associated with it, a prescribed number and type of quality control standards that are analyzed in a prescribed order. The analytical sequence is an important aspect of the analytical work performed because it allows the analyst and subsequent data

reviewers to determine if there are trends in sample results or QC related to the order in which samples were analyzed. This may allow the elimination of unnecessary re-analysis due to a QC failure (cross contamination between samples) during an analytical sequence. Therefore the order in which samples are analyzed will be traceable to the analytical sequence.

The analytical sequence typically starts with either calibration or confirmation that the calibration is still valid. See Table 6-3 for QC sample frequency requirements used during inorganic analysis.

For most inorganic analyses, the analytical sequence ends with a continuing calibration standard and blank. More than one batch of samples can be analyzed in an analytical sequence as long as continuing calibration control is maintained.

6.5.2 Initial Calibration Verification

The initial calibration verification analytical standard (ICV) is used to confirm the accuracy of the calibration and the standards used for calibration. Acceptable performance of the ICV demonstrates that both the standards used and the instrument are functioning properly. The initial calibration verification is prepared from a source other than that used to prepare the calibration standards (see Section 4.0).

Most inorganic techniques are subject to routine, frequent recalibration. The ICV is required whenever the system is recalibrated. The initial calibration verification shall be run following calibration and before analysis of client samples.

Acceptance criteria for major inorganic instrument systems or analyses can be found in Table 6-3. Failure of the initial calibration verification indicates instrument and/or standard problems that must be evaluated and corrected before any client samples are processed for the analytes of interest.

6.5.3 Continuing Calibration Verification

The continuing calibration verification analytical standard (CCV) is used to monitor instrument stability over time. Acceptable performance demonstrates continued appropriateness of the calibration, indicating that the system is still in control. The CCV may be prepared from any reliable source and need not be nationally or internationally traceable. The initial calibration verification standard may also be used as the CCV.

Each inorganic analytical system shall include periodic checks on the stability of the instrument calibration. The CCV acceptance criteria and frequency is discussed in Table 6-3. Failure indicates that the analytical system has drifted out of control and requires corrective action for the analytes of interest. All samples analyzed after the last acceptable continuing calibration verification shall be

reanalyzed. Reanalysis applies to specific analyte failure. In limited cases, isolated analyte failures may be tolerated if sample results still meet the client data quality requirements. Reporting results in such cases requires justification in the report to the client.

6.5.4 Initial and Continuing Calibration Blanks

Initial and continuing calibration blanks monitor effects such as contamination and instrument response drift during routine. The initial/continuing calibration blank is a reagent blank, prepared similarly to the standards but not subjected to preliminary sample preparation except for techniques in which the preparation is an integral part of the analysis. In these cases, the preparation blank or method blank can be considered the equivalent of the initial calibration blank or continuing calibration blank. The generally accepted criteria for these blanks is that they are below the EQL for each analyte of interest. When an analyte exceeds this criteria, analysis shall be investigated for potential impact. Samples with concentrations or activities or activities exceeding the blank contamination level by a factor of 20 or more can be reported unless client requirements dictate otherwise. In all other cases, all samples analyzed since the last acceptable initial calibration blank or continuing calibration blank shall be analyzed for the specific analyte failure.

For inorganic compounds, each initial calibration verification shall be followed by an initial calibration blank and each subsequent continuing calibration verification shall be followed by a continuing calibration blank. This protocol indicates potential carry-over effects (carry over of residual material from one sample to the next in the sequence).

6.5.5 Internal Standards

An internal standard is an analyte that is similar to the analyte(s) of interest in terms of its analytical response, but which is not normally expected to be found in the sample. Internal standards are added to every standard, blank, matrix spike, matrix spike duplicate and sample before analysis. Internal standards are used as the basis for quantitation of the target analytes of interest.

Internal standards are routinely used in inductively coupled plasma spectrometry/mass spectrometry (ICP/MS) analysis although they may be appropriate to other types of analysis. Selecting appropriate internal standards shall be method and analyte list specific because all results are normalized based on internal standard performance. Laboratory procedures shall specify internal standards used and associated acceptance criteria.

6.5.6 Low-Level Standard

The low-level standard is used to monitor instrument performance in the region at or near the EQL and is routinely applied to inorganic systems to monitor sensitivity in the EQL region.

For inductively coupled plasma spectrometry (ICP) systems, the low-level standard should be prepared at approximately two times the EQL. The majority of other inorganic techniques employ a low-level standard that is at or near the EQL. See Table 6-3 for details. In those cases where it is used as part of instrument calibration, a separate low-level standard is not required.

A recovery between 75% and 125% is recommended. If the low-level standards fails to meet this criteria, all client samples whose results are less than 10 times the EQL should be evaluated for impact, and any limitations noted in the report narrative.

Table 6-3. Analytical Requirements for Inorganic Quality Control.

Quality Control Requirements	Frequency	Criteria	Corrective Action
Inductively Coupled Plasma Spectrometry (ICP) and Flame Atomic Absorption			
Initial calibration verification (ICV)	Immediately after calibration (typically mid-point region)	90% to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Continuing calibration verification (CCV)	Every 10 samples and at the end of the run	90% to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Continuing calibration blank (CCB)	After each CCV	<EQL	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Low-level standard[a]	At the beginning of an analysis (but not before ICV and ICB)	Recommended 75% to 125%	Investigate for analyst error. Discuss in narrative.
Interference check standard[b]	After ICV and ICB and before last CCV and CCB	80% to 120%	Investigate failures. Correct. Reanalyze.
Serial dilution	1 per batch of samples prepared	# 10% difference when analyte >10 times IDL after 5 fold dilution	Investigate for source of error. Re-prepare/re-analyze as necessary. Discuss performance in narrative.
Post digestion spike (PDS)	When matrix spike fails or when new or unusual matrix is encountered	Recommended 75% to 125%	Investigate for source of error. Re-prepare/re-analyze as necessary. Discuss performance in narrative.
Inductively Coupled Plasma Spectrometry/Mass Spectrometry (ICP/MS)			

Quality Control Requirements	Frequency	Criteria	Corrective Action
Initial calibration Verification (ICV)	Immediately after calibration (typically mid-point region)	90% to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Continuing calibration verification (CCV)	Every 10 samples and at the end of the run	90% to 110%	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Continuing calibration blank (CCB)	After each CCV	<EQL	Investigate failure for analytes of interest. Correct. Recalibrate for analytes of interest.
Interference check standard	After ICV and ICB and every 12 hours	Monitor for interferences	Investigate. Correct/Reanalyze/Flag.
Serial dilution	1 per batch of samples prepared or when internal standard criteria failure occurs	# 10% difference when analyte > 100 times IDL	Investigate for analyst error. Discuss performance in narrative.
Post spike	When MS fails or when new or unusual matrix is encountered	75% to 125%	Investigate for analyst error. Discuss performance in narrative.
Internal standard	Every sample, QC sample, blank, and standard	30% to 120%	Perform serial dilution. Evaluate. Correct/Report.
Mercury (e.g., Cold Vapor Atomic Absorption-Manual and Automated)			
Initial calibration verification (ICV)	Immediately after calibration	80% to 120%	Investigate. Correct. Reanalyze.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate. Correct. Reanalyze.
Continuing calibration verification (CCV)	Every 10 samples	80% to 120%	Investigate. Correct. Reanalyze and reprepare

Quality Control Requirements	Frequency	Criteria	Corrective Action
			previous 10 samples.
Continuing calibration blank (CCB)	After each CCV	<EQL	Investigate. Correct. Reanalyze and reprepare previous 10 samples.
Low-level standard (LLS)	After ICV and ICB	Recommended 75% to 125%	Investigate for analyst error. Discuss in narrative.
Cyanide (All Techniques)			
Initial calibration verification (ICV)	Immediately after calibration	85% to 115%	Investigate. Correct. Reanalyze.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate. Correct. Reanalyze.
Continuing calibration verification (CCV)	Every 10 samples	85% to 115%	Investigate. Reanalyze previous 10 samples.
Continuing calibration blank (CCB)	After CCV	<EQL	Investigate. Reanalyze previous 10 samples.
Cyanide (All Techniques) (Cont'd)			
Low-level standard (LLS)	After ICV and ICB	Recommended, 75% to 125%	Investigate for analyst error. Discuss in narrative.
Graphite Furnace Atomic Absorption			
Initial calibration verification (ICV)	Immediately after calibration	90% to 110%	Investigate. Correct. Recalibrate.
Continuing calibration verification (CCV)	Every 10 samples and at the end of the run	90% to 110%	Investigate failures. Correct. Recalibrate and/or reanalyze previous 10 samples.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate failures. Correct. Recalibrate and/or reanalyze previous 10 samples.
Continuing calibration blank (CCB)	After each CCV	<EQL	Investigate failures. Correct. Recalibrate and/or reanalyze previous 10 samples.

Quality Control Requirements	Frequency	Criteria	Corrective Action
Low-level standard	After ICV and ICB	Recommended 75% to 125%	Investigate for analyst error. Discuss in narrative.
Graphite Furnace Atomic Absorption (Cont'd)			
Analytical spike	Each sample, preparation blank (PB), method blank (MB), blank spike (BS), or laboratory control sample (LCS) and duplicate	85% to 115%	On PB or BS or LCS corrective action required. Sample results <EQL do not require corrective action unless recovery is below 40%. All else perform either method of standard additions or dilution. Discuss in narrative.
Ion Chromatography			
Initial calibration verification (ICV)	Beginning of each analytical sequence	90% to 110%	Investigate. Correct. Reanalyze.
Initial calibration blank (ICB)	After ICV	<EQL	Investigate. Correct. Reanalyze.
Continuing calibration verification (CCV)	Every 10 samples	90% to 110%	Investigate. Correct. Reanalyze previous 10 samples.
Continuing calibration blank (CCB)	After CCV	<EQL	Investigate. Correct. Reanalyze previous 10 samples.
Low-level standard (LLS)	After ICV and ICB	Recommended 75% to 125%	Investigate for analyst error. Discuss in narrative.
Post digestion spike (PDS)	When matrix spike fails	Recommended 75% to 125%	Investigate for source of error. Re-prepare/re-analyze as necessary. Discuss in narrative.
pH			
Continuing calibration verification (CCV)	After every 10 samples	∀0.1 pH unit	Rerun all samples since last valid CCV
Ion Selective Electrode, Colorimetric, Titrimetric (e.g., Ammonia, Hexavalent Chromium, Fluoride)			

Initial calibration verification (ICV)	Immediately after calibration for working curve technique, prior to analysis of samples for all other techniques.	Based on long-term statistical performance	Recalibrate
Initial calibration blank (ICB)	After ICV	<EQL	Recalibrate
Continuing calibration verification (CCV)	After every 10 samples for working curve technique, at the end of the run for all other techniques.	Based on long-term statistical performance	Rerun all samples since last valid
Continuing calibration blank (CCB)	After each CCV	<EQL	Rerun all samples since last valid

Notes:

[a]This standard equals the estimated quantitation limit standard for flame atomic absorption.

[b]Not required for flame atomic absorption.

EQL = estimated quantitation limit
RPD = relative percent difference

6.5.7 Interference Check Standards

Interference check standards are typically applied in ICP systems (e.g., ICP and ICP/MS). The interference check normally consists of two standards. The first standard contains known concentrations of the major interfering elements that will provide an adequate test of interelement correction factors. The second standard contains both the major interferents and the majority of other analytes tested. The major interferents are spiked into the standards at significant concentrations that are expected to produce an interference effect. All other analytes are spiked at relatively low levels. Data from both standards, when corrected, should recover between 80% and 120% for all analytes tested or an interelement correction is considered inadequate. The first standard, containing only the major interferents of concern, should produce no analyte concentration whose absolute value is in excess of the EQL. Instruments capable of showing negative results do not require the second standard that contains both interferents and additional analytes tested.

6.5.8 Analytical Spike

An analytical spike is a spike that is added to the sample just before analysis (i.e., after preparation). It differs from the matrix spike where the spike is added to the sample prior to sample preparation. The analytical spike is used to gauge instrument and sample matrix performance during the measurement process. Typically, a very small quantity of spike is added so no significant change occurs in sample volume or matrix effects. The concentration spiked should equal 50% to 100% of the sample analyte concentration or approximately two times the EQL if no analyte is expected or the concentration is unknown.

Analytical spikes are required for graphite furnace atomic absorption analysis. They are also used for other analysis, such as uranium by laser fluorimetry, to help determine potential interference effects. The analytical spike is essentially the same as a post digestion spike. However, because the analytical spike is applied to all samples whereas the post digestion spike (see Section 6.5.9) is applied exclusively to the matrix spike sample, different nomenclature is applied.

Recovery of the analytical spike is determined by subtracting the spiked sample concentration from the accompanying sample concentration and dividing the difference by the amount spiked (see Section 7.3.1). Recoveries outside of 85% to 115% warrant investigation and corrective action. Corrective action may consist of dilution followed by reanalysis, the use of standard additions (see Section 6.5.11), or, in extreme cases, re-preparation of the sample followed by reanalysis.

6.5.9 Post Digestion Spike

For inorganic analytes of interest, a post digestion spike (PDS) is a spike added to the sample after preliminary preparation, usually just before analysis. The PDS is used to indicate matrix-related interferences on the analytical system that may still be present in the sample following digestion. The

PDS is normally used when a matrix spike failure occurs.
This technique is typically used for ICP analysis but is appropriate to other analyses as well.

PDS performance can be used to identify problems caused by sample matrix effects during preparation and/or measurement. In the case of unusual matrix effects only during the preparation step, the MS will fail but the PDS will pass. If both the MS and PDS fail, the failure is due to matrix effects in both the preparation and measurement steps.

Acceptable recovery is generally 75% to 125% for the PDS (see Section 7.3.1). If the post digestion spike meets the acceptance criteria indicating that MS failure occurred during the sample preparation step, all client samples in the batch should be flagged in the laboratory report and the sample preparation problem pointed out in the case narrative. If the PDS fails to meet the acceptance criteria, this indicates a failure in both the sample preparation and measure steps caused by matrix problems. All results of client samples in the batch should be flagged and the reasons discussed in the case narrative.

Re-analysis of the samples using different preparation and/or measurement procedures should be considered by the laboratory if alternative procedures are available, which in the judgement of qualified chemists, offer a reasonable solution to the problem(s). Prior to re-analysis, client concurrence must be obtained because the procedural changes may violate mandated existing regulatory or project requirements.

6.5.10 Serial Dilution

Serial dilution is used when new or unusual matrices are encountered as an indicator of potential matrix-related interferences associated with analysis. It is simply a five-fold dilution of a sample (after all preparation steps are complete) followed by analysis. Serial dilution is only performed when a sufficient number of target analyte concentrations exceed 50 times the IDL in the client sample. When sample analyte concentration is less than 50 times the IDL, an analytical spike should be performed.

The serial dilution is designed to indicate potential problems such as high solids effects which can impact sample uptake resulting in analyte measurement differences. In these cases, results would begin to vary beyond the 10% criteria because of sample aspiration and the subsequent effect on analyte species detected. The serial dilution does not replace a sample dilution necessary to maintain a sample in optimum instrument performance range.

A percent difference between the original and diluted sample results of 10% or less indicates no significant matrix effects during the measurement process. The client sample results in the batch which doesn't meet the serial dilution acceptance criteria should be noted and the possible matrix effects discussed in the case narrative.

6.5.11 Method of Standard Additions

The method of standard additions consists of a blank and at least three standards to which aliquots of the sample are added. The standards used should be approximately 50%, 100%, and 150% of the expected sample concentration. The method of standard additions can be used in lieu of instrument calibration because each sample essentially has its own calibration. However, the QC presented in Section 6.4 is still required (including "auto-zeroing" on the calibration blank). The method of standard additions is meant to compensate for a sample matrix effect that enhances or depresses analyte signals.

6.6 ORGANIC PREPARATIVE TECHNIQUES

Preparative techniques are those operations used to prepare a sample for analysis. Examples of preparative techniques include: digestion, dissolution, extraction, phase partitioning, and/or leaching of a sample material. Separation and/or isolation techniques are also considered preparative if performed before analysis, to facilitate reliable analyte measurement. Simple dilution is not considered a sample preparation technique. Selection of preparative techniques should be based upon client data quality requirements. See Table 6-4 for frequency requirements used during preparation.

HASQARD considers the use of either Contract Laboratory Program protocols or associated SW-846 protocols to be acceptable because applicable SW-846 methods are based on early Contract Laboratory Program statements of work (i.e., based on Contract Laboratory Program Statement of Work, July 1985 revision).

6.6.1 Preparation Batch

A preparation batch is a group of samples, of similar matrix type, prepared at the same time. A batch shall not exceed 20 client samples. More than 20 samples can be prepared at the same time, if the required number of QC samples are performed for each batch. If clients do not specify project-specific QC (which requires the laboratory to select client samples for duplicates and matrix spikes), the laboratory may combine up to 20 samples of similar matrix type for preparation with only one matrix spike duplicate (or duplicate) and matrix spike required. In the case of process testing or unique client requirements, QC elements such as a sample duplicate (or matrix spike duplicate) and matrix spike may be performed for every 20 client-specific samples received. However, the preparation blank and laboratory control sample or blank spike requirements are always applied to each batch of samples.

A sample or series of samples which do not require preparation or separation prior to analysis would not fall under the requirements in this section. Additionally, limited sample quantity may limit the laboratory's ability to meet the duplicate and matrix spike requirements. In such cases, alternative approaches should be considered to demonstrate sample precision and accuracy. Unique client requirements shall be documented and agreed upon by the laboratory and the client before work begins.

Table 6-4. Preparative Requirements for Volatile, Semivolatile, and Gas Chromatography Quality Control

Quality Control Requirements	Frequency	Criteria	Corrective Action
Method blank	1 per batch	# EQL (see Section 6.6.2)	Investigate against samples and client DQRs. Correct. Reprepare as required.
Blank spike -or- LCS	1 per batch ---------- 1 per batch	Vendor/method/ statistical (see Section 6.6.3) ---------- Vendor/statistical (see Section 6.6.3)	Investigate, evaluate against DQRs, Correct and Reprepare/reanalyze as applicable.
Matrix spike and matrix spike duplicate (Precision)	1 set per batch	See Section 6.6.5	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Matrix spike and matrix spike duplicate (Accuracy)	1 set per batch	See Section 6.6.4	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Surrogate	Each sample, QC sample, and standard.	See Section 6.6.6	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Total Carbon, Total Inorganic Carbon, and Total Organic Compound			
Duplicate	1 per batch	# 20% RPD when >10 times IDL	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still

			unacceptable, discuss in narrative.
Matrix spike	1 per batch	Recommended 75% to 125%	Evaluate. If lab error, reprepare and analyze. If matrix driven, evaluate against DQRs, notify client if still unacceptable, discuss in narrative.
Blank spike Or Laboratory control sample	1 per batch	80% to 120% or statistical Vendor or statistical	Investigate, Evaluate against DQRs, Correct, Reprepare and analyze as applicable.
Method blank	1 per batch	<EQL	Investigate, Evaluate against DQRs, Correct, Reprepare and analyze as applicable.

Notes:

EQL = estimated quantitation limit
QC = quality control
RPD = relative percent difference.

6.6.2 Preparation Blank (Method Blank)

The sample preparation blank (method blank) is used to monitor contamination resulting from the sample preparation process. The preparation blank is generally distilled or deionized water, which is subjected to the same processing as the samples, including all reagent additions. The laboratory is also free to use a matrix more closely related to the actual samples processed provided the matrix is free of contamination from analytes of interest (e.g. clean soil or sand for solid matrices). Interferences and ancillary contamination produced by the blank material would be expected to be similar to that of the sample.

The preparation blank volume or weight shall be approximately equal to the sample weight or volume being processed and shall be presented in the same context as the samples. The blank should be evaluated for it contribution to the sample, based upon how the sample was prepared. A method blank shall be prepared with each batch of samples processed at the same time.

Preparation or method blank acceptability shall be demonstrated as follows: 1) the blank shall be less than the EQL of the associated samples, or, if the blank is equal to or above the EQL, 2) it shall not exceed 5% of the measured concentration present in the associated samples, or, when a decision level is specified, 3) the blank shall not exceed 5% of the decision level unless 2) above applies. Note: The laboratory must be capable of achieving an EQL less than or equal to 5% of the Decision Level or must negotiate an acceptable alternative.

As a special requirement, the concentration of the following analytes shall be less than five times the EQL.

methylene chloride.

acetone.

2-butanone.

phthalate esters.

All samples in the preparation batch will be re-prepared and re-analyzed if the preparation blank (method blank) fails to meet one of the acceptance criteria for an analyte of interest unless client data quality requirements dictate otherwise. The client shall be notified prior to repreparation if additional costs will be incurred.

The results of the preparation blank analysis should be reported to the client as a part of routine reports. Preparation blank results are not subtracted from sample results unless client data quality requirements specify otherwise, in which case the narrative accompanying the results should state that blank

subtraction was used.

Preparation blanks or method blanks shall be prepared with each batch of samples.

6.6.3 Laboratory Control Sample or Blank Spike

A laboratory control sample (LCS) or blank spike (BS) is used to monitor the effectiveness of the sample preparation process. The laboratory control sample is a material similar in nature to the sample being processed containing the analyte(s) of interest (e.g., standard reference material). A laboratory control sample, if available, shall be prepared with each batch of samples processed at the same time. The blank spike is distilled or deionized water or other suitable substrate spiked with the analytes(s) of interest. A blank spike is normally used when an appropriate laboratory control sample is unavailable. For organic preparations, the method blank, spiked with surrogates, can be used to meet the BS requirement.

Blank spike control is demonstrated by target analytes being within either the preset limit of 80%-120% or, within statistically determined limits when the ∀20% criteria cannot be reliably achieved.

Laboratory control sample acceptability is demonstrated by target analytes being within established control or tolerance limits. Control limits are either provided by the vendor or statistically determined by multiple analyses over time. For the LCS, the vendor supplied precision may effect the tolerance limits applied to the analyte.

All samples in the preparation batch shall be re-prepared and analyzed for those analytes in which the acceptance criteria for the LCS or BS has not been met. In limited cases, results may be acceptable for reporting provided the lab can demonstrate that the client DQR was still achieved. The client shall be notified prior to repreparation if additional costs will be incurred.

A laboratory control sample or BS shall be prepared with each batch of samples and the results reported to the client. No adjustment of client sample results based on LCS or BS recovery is made in the laboratory report.

6.6.4 Matrix Spike

A matrix spike is a client sample that has been spiked with the analyte(s) of interest and processed in the same manner as the sample. The matrix spike is used to monitor method performance in a specific sample matrix. Matrix spike results are a measure of the bias (difference from true value) in the measurement of the target analytes introduced by the client sample matrix.

When the sample concentration is unknown, spiking is typically performed at a level that is one of the following: 1) equivalent to the regulatory threshold, 2) specified by method, or 3) 1 to 5 times the EQL. Otherwise, the spiking should be performed at a level equivalent to 1 to 2 times that of the sample. When the concentration of the analyte in the original sample is greater than 0.1%, no matrix spike is required.

For organic analysis, matrix spike control is demonstrated when target analytes are within established control limits. The control limits identified "USEPA Methods for Evaluating Solid Waste, Physical/Chemical Methods" (SW-846) or the current Contract Laboratory Program statement of work are acceptable. The selection of limits are based on which method (SW-846 or Contract Laboratory Program) the laboratory uses. Control limits are established by one of the following: 1) regulatory requirement, 2) the client via data quality requirements for a particular project or program, or 3) laboratory performance over time. For compounds of interest or matrices not covered by SW-846 or the Contract Laboratory Program, the laboratory shall establish spike compounds, spike levels, and acceptable recovery criteria according to Volume 1, Section 4.0.

If the matrix spike recovery fails to meet criteria, the batch shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix and represented by matrix spike performance, are adequately portrayed and discussed in the report to the client.

In those instances where the sample concentration significantly exceeds the amount of spike added in the prepared samples, the data must be further evaluated to determine if the recovery of the spiked sample is meaningful.

A matrix spike shall be prepared with each batch of 20 samples and the results reported to the client along with the calculated recovery (see Section 7.3.1). No adjustment of the client sample results is made in the laboratory report.

6.6.5 Laboratory Sample Duplicate or Matrix Spike Duplicate

Laboratory sample duplicates are two aliquots of the same sample (intralaboratory split) that are taken through the entire sample preparation and analytical process. Laboratory duplicates are used to assess the precision of the preparation and analysis process in a client-specific matrix. Agreement between

duplicates indicates the reproducibility of the combined preparation,separation, and measurement process (precision).

Matrix spike duplicates are two spiked aliquots of the same sample that are taken through the entire sample preparation and analytical process. In cases where the sample is not expected to contain reasonable concentrations of the analytes of interest, duplicate sample results will not provide a reliable estimate of precision. In these cases, matrix spike duplicates are used to demonstrate analytical precision in the client sample.

The degree of agreement between duplicates indicates reproducibility of the combined preparation/ separation, and measurement process (precision).

Disagreement can occur due to analyte concentration differences within the sample matrix (non-homogeneity) that are not amenable to analyst control during the analytical process. Disagreement may aries if the method has poor applicability to the analyte/matrix tested. Typically, organic analyses include a matrix spike and matrix spike duplicate because a low probability exists that the majority of those analytes of interest will be detected in the sample.

Organic duplicate RPD criteria vary widely according to analyte and method. They are very method/matrix dependent. Acceptance criteria are established by one of three procedures: 1) specified by regulatory requirement, 2) specified by the client via the DQO process for a particular project, 3) laboratory performance over time for samples with similar matrices and concentration ranges.

One set of matrix spike/matrix spike duplicates is required for each batch of samples. Precision is calculated using the RPD (Section 7.2.2). Additional replicates may be performed if requested by the client. These additional samples will increase the likelihood of detecting non-uniformly distributed analytes in the client sample. It will also allow for a more accurate estimate of the variability of the overall analytical performance on client-specific sample matrices. When more than two replicates are used, precision is expressed in terms of the relative standard deviation (Section 7.2.1)

The results of duplicate (or matrix spike duplicate) analyses are reported to the client along with the calculated RPD for each analyte.

6.6.6 Surrogates

A surrogate is a compound or analyte that is added to all samples (both client samples and QC samples) prior to preparation. The surrogate is typically similar in chemical composition to the compound or analyte being determined, yet not normally encountered in most samples. Surrogates are expected to respond to the preparation and measurement systems in a manner similar to the analytes of interest.

Criteria for selection and recovery of surrogates is generally specific to the method and compounds being detected. Each method that uses surrogates shall specify instructions for surrogate introduction and use. For organic analysis, surrogate control is demonstrated when they are within established control limits. Control limits are established by one of the following: 1) regulatory requirement, 2) the client via data quality requirements for a particular project or program, or 3) laboratory performance over time.

Surrogate recoveries are reported as measured (i.e., no sample recovery corrections are performed based on surrogate recovery). Because surrogates are added to all standards, samples, and QC, they are a useful tool in evaluating overall method performance in a given matrix. If surrogate recovery fails to meet criteria, the sample results shall be investigated for sources of error. Re-preparation and/or re-analysis should be conducted as necessary based on the DQO/DQR. The goal is to ensure that limitations on the data caused by the sample matrix and represented by surrogate performance, are adequately portrayed and discussed in the report to the client.

6.7 ORGANIC ANALYTICAL TECHNIQUES

Analytical techniques are considered those operations which permit the measurement of a parameter of interest. Analysis could be considered measurement of some property for which there is an instrument response that can be related to the concentration or amount of the substance of interest in a sample or in some material prepared from the sample. The QC requirements presented below are designed to verify and document proper instrument operation and to give the analyst information regarding the precision, accuracy, and sensitivity of the analytical process. Selection of analytical technique should be based upon client data quality requirements. HASQARD considers the use of either Contract Laboratory Program protocols and associated SW-846 protocols to be acceptable because applicable SW-846 methods are based on early Contract Laboratory Program statements of work (i.e., based on Contract Laboratory Program Statement of Work July 1985 revision).

6.7.1 Analytical Sequence (Run)

An analytical run or sequence is defined as a group of samples analyzed together that may include one or more preparation batches. Each analytical sequence has associated with it, a prescribed number and type of quality control standards that are analyzed in a prescribed order. The analytical sequence is an important aspect of the analytical work performed because it allows the analyst and subsequent data reviewers to determine if there are trends in sample results or QC related to the order in which samples were analyzed. This may allow the elimination of unnecessary re-analysis due to a QC failure (cross contamination between samples) during an analytical sequence. Therefore the order in which samples are analyzed will be traceable to the analytical sequence.

The analytical sequence typically starts with either calibration or calibration verification to confirm the calibration is still valid. See Tables 6-5 through 6-8 for QC sample frequency requirements used during organic analysis. The run ends based on analytical clock expiration for organic analyses by GC/MS. For the gas chromatography and carbon analysis, the run ends based upon continuing calibration performance.

6.7.2 Initial Calibration Verification

The initial calibration verification is a standard used to confirm the acceptability of the calibration and the standards used to prepare the calibration. Acceptable performance of the initial calibration verification demonstrates that both the standards used and the instrument are functioning properly. The initial calibration verification is prepared from a source other than that used to prepare the calibration standards (see Section 4.0).

Analytical measurement systems for which calibration applies over an extended period of time (i.e., months for some GC/MS methods) normally use the initial calibration verification only at the time of calibration. Subsequent, routine performance checks are made using the equivalent of a continuing calibration verification (see Section 6.6.3).

Analytical measurement systems that are calibrated frequently and for which calibration standards are routinely prepared normally follow calibration with an initial calibration verification.

Acceptance criteria for major instrument systems or analyses can be found in Tables 6-5 through 6-8. Failure of the initial calibration verification indicates instrument and/or standard problems that shall be evaluated and corrected before any samples are processed for the analytes of interest.

Table 6-5. Analytical Requirements for Volatile Quality Control (Gas Chromatography/Mass Spectrometry).

Quality Control Requirements	Frequency	Criteria	Corrective Action
Tune	Once on a 12-hour clock	See Section 4.0	Investigate. Correct.
Continuing calibration check	Once on a 12-hour clock	See Sections 4.0 and 6.7.3	Investigate. Correct. Reanalyze.
Internal standard	Each sample, quality control sample, blank, and standard	See Section 6.7.5	Reanalyze or reprepare as appropriate.
Qualitative identification	Each sample	Compare to spectra generated and retention times	Report any unusual circumstances in narrative.
Quantitation	Each sample. See also Section 4.0 for surrogate and internal standard.	Calculate off continuing calibration	Report any unusual circumstances in narrative.

Table 6-6. Analytical Requirements for Semivolatile Quality Control (Gas Chromatography/Mass Spectrometry).

Quality Control Requirements	Frequency	Criteria	Corrective Action
Tune	Once on a 12-hour clock	See Section 4.0	Investigate. Correct.
Continuing calibration check	Once on a 12-hour clock	See Sections 4.0 and 6.7.3	Investigate. Correct. Reanalyze.
Internal standard	Each sample, quality control sample, blank, and standard	See Section 6.7.5	Investigate. Correct and reanalyze or reprepare.
Qualitative identification	Each sample.	Compare to spectra generated and retention times	Report any unusual circumstances in narrative.
Quantitation	Each sample. See also Section 4.0 for surrogate and internal standard.	Calculate off continuing calibration	Report any unusual circumstances in narrative.

Table 6-7. Analytical Requirements for Gas Chromatography

Quality Control Requirements	Frequency	Criteria	Corrective Action
Continuing calibration verification	Routinely during run according to method	As per method, evaluate for retention time and area response	Investigate. Correct. Reanalyze.
Continuing calibration blank	Routinely, following continuing calibration verification according to method	Evaluate for carryover and contamination	Investigate. Correct. Reanalyze.

Table 6-8. Analytical Requirements for Total Carbon, Total Inorganic Carbon, and Total Organic Compound Quality Control

Quality Control Requirements	Frequency	Criteria	Corrective Action
Continuing calibration verification	Every 15 samples	85% to 115%	Rerun previous 15 samples
Continuing calibration blank	After each continuing calibration verification	<EQL	Rerun previous 15 samples

Notes:

EQL = estimated quantitation limit.

6.7.3 Continuing Calibration Verification

The continuing calibration verification analytical standard (CCV) is used to monitor instrument stability over time. Acceptable performance demonstrates the continued accuracy of the calibration. The CCV may be prepared from any reliable source. The initial calibration verification QC sample may be used as the CCV sample.

The calibration of organic analytical GC/MS methods is limited by analytical run time. Each run is defined by a 12-hour clock that cannot be exceeded. Each run starts with a continuing calibration verification (after tuning). The analyst shall rely on internal standard and surrogate performance to ensure that the sample run ended in control. Corrective action, such as reanalysis of all samples demonstrating unacceptable internal standard performance, shall be taken.

Analytical runs for organic analysis such as GC typically can extend anywhere from several hours to several days. Continuing calibration checks are required throughout the runs duration (e.g., approximately every 10 samples for SW-846, every 12 hours for Contract Laboratory Program). Total organic carbon, total inorganic carbon, and total carbon measurements should also include continuing calibration verification checks every 15 samples.

All samples analyzed after the last acceptable continuing calibration verification (see Tables 6-5 through 6-8) shall be reanalyzed. Reanalysis applies to specific analyte failure.

6.7.4 Continuing Calibration Blank

Continuing calibration blanks (i.e., instrument blanks) monitor effects such as contamination and instrument response drift. The continuing calibration blank is a reagent blank prepared similarly to the standards but not subjected to preliminary sample preparation except for techniques in which the preparation is an integral part of the analysis (i.e. purge and trap procedures). In these cases, the preparation blank or method blank can be considered the equivalent of the initial calibration blank or continuing calibration blank. The generally accepted criteria for reagent blanks is that they are below the EQL for each analyte tested. When an analyte exceeds this criteria, the analysis shall be investigated for potential impact. Samples with target analyte concentrations exceeding the blank contamination level by a factor of 20 or more can be reported unless client requirements dictate otherwise. In all other cases, all samples analyzed since the last acceptable initial calibration blank or continuing calibration blank shall be reanalyzed for the specific analyte failure.

Several organic compounds are more readily introduced into blanks; see Section 6.6.2 for these specific exceptions. In the case of organic analysis by GC/MS, the blank is typically the equivalent of the method blank. The method blank is run after the continuing calibration verification standard. Periodic calibration blanks are not performed. In the case of organic analysis by gas chromatography and

carbon analysis, periodic blanks are recommended following each continuing calibration verification.

The continuing calibration blank problems should be corrected and the samples run after the last successful continuing calibration blank should be re-analyzed.

6.7.5 Internal Standards

An internal standard is an analyte that is similar to the analyte(s) of interest in chemical composition and analytical response but which is not normally expected to be found in the sample. Internal standards are added to every standard, blank, matrix spike, matrix spike duplicate, and sample before analysis. Internal standards are used as the basis for quantitation of the analytes of interest.

Selecting appropriate internal standards shall be method- and compound-list specific because all results are normalized based on internal standard performance. Laboratory procedures shall specify acceptance criteria. See Volume 1, Section 4.0.

Internal standards are used in organic GC/MS analysis although they may be appropriate to other types of analysis. Generally, area counts falling <50% or >150% of original area counts in the continuing calibration standard are considered unacceptable.

6.7.6 Low-Level Standard

The low-level standard is used to monitor instrument performance in the region near the EQL. When the low-level standard concentration is included in the instrument calibration, a separate low-level standard is not required. Low-level standards are not required for total organic carbon, total inorganic carbon, and total carbon.

6.8 PHYSICAL TESTING

Quality control specifications for several physical tests are provided in Table 6-9.

Table 6-9. Physical Testing Quality Control (Differential Scanning Calorimetry, Thermogravimetric Analysis, and Differential Thermal Analysis/Thermogravimetric Analysis).

Quality Control Requirements	Frequency	Criteria	Corrective Action
Continuing calibration verification (performance check) temperature characteristics	Each time the temperature ramp rate is changed	Standard(s) which is within the range of analysis and thermogravimetric analysis standard (material of known thermal properties) shall conform to known physical constants.	Investigate. Correct and restart. Recalibrate if necessary.
Continuing calibration verification (performance check) mass/weight characteristics	Periodically, not to exceed quarterly	Check balance performance using material of known mass or of known mass loss as a function of temperature properties	Investigate. Correct. Restart. Recalibrate if necessary.

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7.0 COMMON DATA QUALITY CALCULATIONS

This section provides various formulas that are typically employed to compute QC parameters that are used to assess data quality. These quality control parameters should be monitored, evaluated, and/or trended on a short-term and long-term bases. For example, system contamination control (blank or background activity), precision, accuracy, spike recovery, tracer or carrier yield recovery could be evaluated based on method, matrix, and activity or concentration level. Such activities provide a basis for continuous quality improvement and insight on overall laboratory performance.

7.1 PRECISION

Precision has been defined in Section 1.0. Sample precision is estimated by using duplicates, matrix spike duplicates or replicates. Samples used to calculate precision should contain concentrations of the analytes of interest above the MDC or EQL. The precision of a method in a given matrix is expressed as the relative standard deviation (RSD) or the relative percent difference (RPD).

In addition to precision determined by the sample duplicate or matrix spike duplicate, precision for the standards (e.g. laboratory control sample, continuing calibration verification standard) can be calculated and used to monitor quality control of the analytical measurement system over time. Precision of the sample can also be monitored for long-term quality control, but should be based on method, matrix, and activity/concentration in the sample.

7.1.1 Relative Standard Deviation

The RSD is used when at least three replicate measurements are performed on a given technique. The RSD is computed using the following equation:

$$RSD = \frac{s}{\bar{x}} * 100$$

where

s	=	Standard deviation with n - 1 degrees of freedom
n	=	Total number of observed values
$\bar{x}$	=	Mean of observed values.

7.1.2 Relative Percent Difference

The RPD is used when two measurements exist. The RPD is generally used to express the precision of duplicate or spike duplicate samples. The RPD is computed using the following equation:

$$RPD = \frac{|x_1 - x_2|}{\bar{x}} * 100$$

where

$x_{1,2}$ = Observed values
$\bar{x}$ = Mean of observed values.

7.2 ACCURACY

7.2.1 Method Accuracy Based on Sample Spike

Accuracy has been defined in Section 1.0. Accuracy for the sample is expressed as the percent recovery (%R) of a matrix spike (or matrix spike duplicate) sample. The percent recovery is calculated based on the following equation:

$$\%R = \frac{(SSR - SR)}{SA} * 100$$

where

SSR = Spiked sample result
SR = Sample result
SA = Spike added

7.2.2 Method Accuracy Based on Standard

The accuracy of an analytical method is expressed as the percent recovery of a standard (%R). The percent recovery of a standard is calculated according to the following equation:

$$\%R = \frac{A_m}{A_k} * 100$$

where

A_m = Measured value of the standard analyte
A_k = Known value of the standard analyte.

Method accuracy obtained from either a sample spike or from a standard can be used to monitor quality control of the analytical measurement system over time. Sample accuracy should be tracked based on the method, matrix, and activity/concentration when it is used for long-term quality control monitoring.

7.3 YIELD RECOVERY (Radiochemistry only)

Yield percent recovery (%Y) of a tracer or carrier in radiochemical analysis is a measure of the effectiveness of separation methods for some radionuclides. It is expressed as the percent recovery and is generally used to correct the analyte recovery in the sample for radiochemical analysis. Yield percent recovery is calculated according to the following equation:

$$\%\,Y = \frac{T_m}{T_k} * 100$$

where

T_m = Measured value of the tracer or carrier
T_k = Known value of the tracer or carrier.

Yield percent recovery should be evaluated per procedure to monitor the effectiveness of the radionuclide separation. If tracer or carrier is not used on every sample, a historic yield percent recovery should be used as the correction factor for the sample analyte.

7.4 MEASURES OF AGREEMENT

7.4.1 Percent Difference

The percent difference (%D) is often used to compare one reference point to another (e.g., average RF from initial calibration compared to RF from continuing calibration listed in Section 7.1.2). The percent difference is calculated using the following equation:

$$\%\,D = \frac{|I - C|}{I} * 100$$

where

I = Observed value used as the reference point

C = Compared value.

7.4.2 Bias

Bias (B) is often used to measure the deviation of a measured value from a known value or accepted reference value. Bias can be assessed by comparing a measured value to an accepted reference value in a sample of known concentration or by determining the recovery of a known amount of analyte of interest spiked into a sample. Thus, the bias caused by the matrix effects based on a matrix spike is calculated using the following equation:

$$B = (X_s - X_u) - K$$

where

X_s = Measured value (e.g., spiked sample)
X_u = Miscellaneous contribution (e.g., sample contribution)
K = Known value (e.g., true spiked value).

If no miscellaneous contributions exist, X_u would be zero.

7.4.3 Mean Difference

Mean difference may be used to compare two duplicate results and is generally used for radiochemical analysis. The mean difference takes into account the uncertainty associated with each measurement. The mean difference is compared based on a two-sided z-test for a known population (Steel and Torrie 1960) and is calculated using the following equation:

$$MD = \frac{|R_1 - R_2|}{\sqrt{(a_1^2 + a_2^2)}}$$

where

R_1 = First sample result
R_2 = Second sample result
a_1 = One sigma uncertainty of first result
a_2 = One sigma uncertainty of second result.

If the MD is greater than or equal to 1.96, a 95% confidence exists that the two results are not equal.

7.5 DETECTION LIMIT CONSIDERATIONS

Detection limit determinations are performed to give the laboratory, and subsequently the data user, information regarding the reliability of low-level results reported. A variety of approaches may be used, each of which portrays method sensitivity at low concentrations differently. This section describes several typical detection limit determinations. Each laboratory shall document which approach it employs and describe how the determination is applied (i.e., performed in sample matrix or performed using low-level standards).

7.5.1 Inorganic and Organic Methods

7.5.1.1 Method Detection Limit. The MDL is defined as "the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is greater than zero" (SW-846, consistent with the requirements specified in 40 CFR 40 Appendix B to 40 CFR 136) and is briefly described in the following text.

The concentration of the MDL for the analyte of concern can be estimated by using one of the following:

An instrument signal-to-noise ratio within the range of 2.5 to 5

The region of the standard curve where there is a significant change in sensitivity (i.e., a break in the slope of the standard curve).

When determining the MDL, a minimum of three analyses are required in a matrix spiking with the analyte of interest at a concentration three to five times the estimated MDL. Whenever possible, the matrix should be the same as or very similar to the sample matrix. All sample processing steps of the analytical method shall be included in the final determination of the MDL.

Variance (S^2) is determined from the replicate measurements, as shown:

$$S^2 = \frac{1}{(n-1)} \left[\sum_{i=1}^{n} (X_i - \overline{X})^2 \right]$$

where

X_i = With measurement of the variable X
= Mean of observed variable X.

The MDL should be determined by the following equation:

$$MDL = t_{(n-1, \alpha = .99)} * (s)$$

where

$t_{(n-1, \alpha=.99)}$	=	One-sided t-statistical value appropriate for the number of samples used to determine standard deviation
s	=	Standard deviation obtained from the MDL replicate measurements.

Each laboratory shall document its approach when employing the MDL determination. The term MDL shall only be employed when all method steps (sample preparation through analysis) are tested. The laboratory shall also document whether the determination was performed using client samples or standards. Results falling below the MDL should be reported as not detected.

7.5.1.2 Instrument Detection Limit. IDL is determined by spiking reagent water with each analyte of concern. The following considerations apply to the selection of the IDL standard:

Concentration of the IDL standard should be at least equal to or in the same concentration range as the estimated IDL

Concentration of the IDL standard should be in the region of the standard curve where there is significant change in sensitivity.

A minimum of seven aliquots of the IDL standard are required to determine the IDL. The IDL standards are run through the analytical process only. The IDL is calculated the same as the MDL. In cases such as some organic analysis and mercury and cyanide determinations, the IDL standard should be subjected to preliminary extraction, digestion, and/or distillation. Each laboratory shall document whether the IDL includes the entire method (i.e., sample preparation through analysis) or only the analytical process. Results falling below the IDL should be reported as not detected.

7.5.1.3 Estimated Quantitation Limit. The estimated quantitation limit (EQL) is the lowest concentration of an analyte that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The analyte concentration at the estimated quantitation limit is determined using the following guidance: 1) 5 to 10 X MDL or IDL, or 2) the lowest non-zero standard in the calibration curve.

Each laboratory shall document the approach used to determine the EQL. EQLs reported with client data shall reflect all method dilution factors (i.e., dilution factors resulting from sample preparation).

Results falling between the IDL (or MDL) and the EQL should be reported with appropriate qualification (e.g., flag, footnote).

7.5.2 Radiochemistry Methods

7.5.2.1 Decision Level Count Rate. The decision level count rate (DLR) is defined as a 95% confidence limit for a critical decision level. This level is used for making a decision as to whether a sample emits radiation above the appropriate blank background level. The decision should be based solely upon whether the net count rate observed for that sample exceeds this DLR. The DLR is calculated as shown below:

$$DLR = 1.65 * \sqrt{\frac{R_b}{T_b} + \frac{R_s}{T}}$$

where

R_b	=	Background count rate
R_s	=	Sample count rate
T	=	Sample count time
T_b	=	Background count time.

When counting a sample containing no analyte (radionuclide) of interest, R_s is assumed to be equal to R_b. The DLR can be simplified as shown below:

$$DLR = 1.65 * (S_b) * \sqrt{2}$$

where

S_b	=	Standard deviation of background (or appropriate blank) count rate for the counting time (T).

For the purpose of interpreting whether an individual sample measurement is different from its appropriate blank, it is recommended that the laboratory compare the net sample count rate with a decision level count rate calculated using the sample specific "appropriate" blank. The "appropriate" blank should include measurement interferences from impurities (e.g., elevated compton continuum, channel crosstalk from higher energy alpha particles measured by liquid scintillation) that are not typically known *a priori* or included in the nominal *a priori* DLR limit. This "true" decision level for the sample is different from the nominal *a priori* decision limit. For some measurement processes, the determination of the "true" appropriate blank for each sample may be impractical. However, every effort should be taken to properly assess the parameters of the appropriate blank.

7.5.2.2 Minimum Detectable Activity. The minimum detectable activity (MDA) has been defined as a level of activity that is practically achievable by a measurement system. The sample MDA generally is applied as the mean (expected) activity of samples having a 5% probability of escaping detection and 5% probability of false detection. The MDA is calculated based on Currie's (1968) formula and is

simplified to the following two equations when the counting time in the sample is the same as in the background.

$$MDA = [(\frac{2.71}{T}) + (2 * DLR)] / K$$

or

$$MDA = [(\frac{2.71}{T}) + (4.65 * S_b)] / K$$

where

T	=	Sample count time
K	=	Detector calibration factor (e.g., count rate/disintegration rate)
S_b	=	Standard deviation of background count rate for the counting time (T).

When T_b is not equal to T_t, MDA is calculated as shown below.

$$MDA = \underline{2.71 + 3.3} \frac{\sqrt{(R_b * T_b) * \left(1 + \frac{T_b}{T_t}\right)}}{x * b * T_t * k}$$

where

R_b	=	Background count rate
T_b	=	Background count time
T_t	=	Sample count time
ξ	=	Counting efficiency
b	=	Abundance
k	=	conversion factor to convert to desired units.

The minimum detectable concentration (MDC) is defined as the mean concentration of samples having a 5% probability of escaping detection and 5% probability of false detection.

$$MDC = \frac{MDA}{q * Y * decay}$$

where

q = Sample quantity (e.g., g or mL)
Y = Chemical yield
decay = Decay factor (correction for radioactive decay to reference date).

Software provided by vendors may have variations of the above formula. A vendor- provided software or data reduction package is adequate for data calculation.

7.5.2.3 *A Priori* and *A Posteriori* Concepts and Information. Decision level count rate, MDA, and MDC are considered as *a priori* (before the measurement). The estimation of these quantities requires specification of nominal values of a number of parameters (e.g., background count rate, count time, estimated interferences, chemical recoveries, decay times). The true appropriate blank for a measurement process includes estimates of the nominal levels of any interferences that may be present in a sample batch.In a number of situations, regulatory limits or contract specifications may require that the measurement process meet or exceed certain MDC limits for the sample batch of interest. Because these determinations require that some preliminary measurements be made, one finds that the assessment of *a priori* detection limit parameters for future measurements may require the knowledge of *a posteriori* information concerning the nominal characteristics of the sample batch gained from preliminary measurements.

The question of whether the sample contains net activity is best answered by comparing the measurement result to the decision level or considering the confidence interval for the measurement result, not by comparing the result to the estimated MDA or MDC.

7.5.3 Limit of Detection

In some cases, the limit of detection is used. The limit of detection is defined as an analyte signal that is three times the standard deviation of its measurements above the corresponding well-characterized blank response (Keith 1991).

The limit of detection represents a criterion for detection decision, i.e., deciding whether to classify a result as detected or not detected when the observed signal is close to that obtained for blank measurements (i.e., similar to background noise).

7.6 UNCERTAINTY

Uncertainty is expressed as the range of values in which the true value is estimated to lie. The uncertainty estimate consists of two components, systematic and random variability. Each contributing source of uncertainty is expected to be distributed over its range. Each systematic component can be estimated in terms of the measurement result for the contributing source of uncertainty. The analytical systematic component can be estimated using standard or spike recovery. The random analytical

component can be estimated from replicate measurements of a sample. The total uncertainty is calculated as the square root of the sum of the squares of random and systematic variabilities as shown in the following equation. The component of uncertainty has to be expressed in the same unit designation (e.g., concentration percentage).

$$\text{Total uncertaint } y = \sqrt{(s_x^2) + \sum_{j=1}^{q} d_j^2}$$

where

s_x	=	Standard error
q	=	Number of systematic uncertainty component
δ	=	Systematic uncertainties.

Uncertainty is commonly used in the radiochemical analyses to express method and counting error. The total random uncertainty is obtained by propagating the individual variance (s_i^2) and is expressed as the standard error based on multiple determinations of x. However, the typical radiochemical methods used are not sufficient to separate systematic and random uncertainties such that biases can be corrected. Uncertainty will be measured, or uncertainty will be estimated if it cannot be measured.

7.7 CONTROL CHARTS

Control charts provide the analyst with early warning of impending problems in a preparative or analytical method. Each laboratory shall document its policy regarding the use of control charts. The laboratory's policy shall articulate the manner in which it will deal with statistical outliers. Blank spike/laboratory control sample performance for all routine preparations shall be monitored via control charts. Radiochemical laboratories shall also monitor calibration verification standards (i.e., counter control standard for radiochemistry). In those cases where the analytical technique involves a large number of analytes (e.g., ICP, GC/MS) the laboratory may select a subset representative of the total for control charting. Additional information on the application, development, and use of control charts can be found in the Ecology manual entitled, *Procedural Manual for the Environmental Laboratory Accreditation Program*. Tabulation of performance statistics can be used in lieu of a control chart.

Laboratories shall document and apply procedures for estimating uncertainty. The rigor associated with the protocol will depend upon the relative contribution from each source of error. When a laboratory implements an industry-recognized method which already specifies the limits for major sources of uncertainty then the laboratory would meet this requirement providing it reported results consistent with the method. In such cases the major sources of uncertainty would still be provided to the client (e.g., in terms of sample precision and accuracy results).

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8.0 DATA ASSESSMENT AND VALIDATION

This section describes the data requirements and specifications between the laboratory and the client, allowing for successful data validation when required by a project or program. This section explains how data validation is integrated into the overall data assessment and DQO planning process. It is not meant to provide users with route validation protocols, instead it provides guidance in the utilization of the tools to build an effective validation and assessment protocol based upon the data quality requirements for a specific client-directed work activity.

8.1 DATA ASSESSMENT PROCESS

Data quality is assessed in two steps. The first step is data validation, traditionally an independent review of laboratory and field data to assure that the procedures, protocols and client specific requirements were correctly followed. The second step in the assessment process is a general data quality assessment. This includes a review to verify the following:

Assumptions made during the planning process were accurate

Sampling and analytical variability identified in the DQO planning process was met

Data make sense

Suitability of the data for making decisions.

In addition, the overall data assessment determines the following:

Any anomalies in the data were addressed and that further sampling and analysis were performed to confirm or negate the anomaly

If corrective actions or a new assessment strategy is required.

8.2 PLANNING CONSIDERATIONS

A common problem is that validation and assessment of data are planned "after the fact" or after the data are collected. This sometimes results in the deliverables from the sampling and laboratory analysis being insufficient (e.g., disorganized, inadequately documented) for complete assessment of the data. The cost of validating poorly planned and insufficient data reports will increase the original laboratory analysis costs.

The problem is compounded when methods other than the Contract Laboratory Program protocols are specified. The Contract Laboratory Program methods have published validation criteria, while the other methods do not. The QC differs between the various methods. For example, the most recent Contract Laboratory Program GC/MS method for semivolatile organic compounds requires that all compounds except five have minimum response factors, while the SW-846 methods use four compounds to verify minimum response. This difference may be significant in the final outcome of the validation process for semivolatile organic compounds.

When non-Contract Laboratory Program methods are used, a qualified person shall write a validation procedure(s). The validation procedure needs to be flexible enough to be adapted to include criteria from the project data requirements. For example, the need to generate accurate data from a background sample is critical because many decisions shall be based on the results from that data. If one were using the SW-846 GC/MS methods, modifying the method and the data validation criteria to ensure that all compounds determined exhibit minimal response in calibration may be appropriate. Once validation procedures are prepared, the procedure shall be provided to the laboratory, such that they know how the data will be evaluated.

Planning assures that the validation and assessment criteria are reflected in the methods used to collect and analyze the samples. This will ensure that any data flags or qualifications are based on the QC and not because of a lack of deliverables or inconsistency between validation requirements, deliverables, and methods.

Planning should also result in specification of methods, which are validation and assessment procedures that reflect the requirements generated during the DQO planning process. The DQO planning process generates the following: 1) the decision rules, 2) the level of uncertainty that the decision maker is willing to accept, and 3) the decisions that shall be made. The level of uncertainty shall dictate the amount of false positives and/or false negatives that the decision maker is willing to accept. This information shall be provided to the laboratory, validators, and data management staff before project initiation.

8.3 ASSESSMENT AND VALIDATION

The assessment and validation process should identify potential false positives and false negatives. Additionally, the DQO planning process should detail the analytes and the action levels for each media.

The analytes and action levels drive the detection limits and, thus, the methods. The validation and assessment should reflect these requirements.

During the planning phase, the laboratory should receive the following information:

Analyte(s) of interest

Any analyte(s) driving risk assessment or the overall decision

Matrices to be sampled

Action or regulatory levels (thresholds)

Level of uncertainty the decision makers will accept (e.g., false positives, false negatives, and confidence level)

Precision and accuracy requirements

Sample locations and site history

Suspected or known contaminants, based on site history or previous data

Number of samples for analysis by matrices and collection schedule

Budget and resources

Any method requirements specified by EPA or Ecology

Data deliverables required including electronic deliverables.

In response to the above information, the laboratory should provide the following information:

Analyte(s) measured by method, including method number or name and revision date for each matrix

Detection limits (organic and inorganic) or estimated minimum detectable activities (radiochemistry)

Accuracy and precision in the matrix or a similar matrix in question

Copies of the laboratory procedures used

QC samples required by the laboratory, such as method blanks, matrix spikes, and duplicates

Sample volume, preservation, and container requirements

Format in which the data will be presented, including electronic and hard copy.

An agreement should be reached between the analytical services provider and the client as to who shall validate the data, what data shall be validated, who shall write the validation procedure, and how the data shall be sent to the validator. The laboratory and the client should agree on the data format and the validation criteria before samples are collected.

Before beginning sample collection, the validator or the validator and the laboratory should document the validation procedure. A qualified laboratory representative should review the validation procedure to assure that the laboratory is capable of meeting the requirements specified. The following areas should be assessed in the validation procedure:

Calibration

Continuing calibration

Method blanks, instrument blanks, and/or backgrounds

Duplicates

Matrix spikes and/or tracer or carrier yields

Laboratory control samples

Holding times

Identification of analyte(s) of interest

Interferences

Quantitation criteria

Instrument performance and counter efficiency

Criteria for validation of detection limits

Criteria for accuracy and precision assessment.

For organic compound analyses, the following areas should be addressed in addition to the previously stated items:

Surrogates (used to assess accuracy)

Tuning (used for GC/MS only)

Lower area limits for minimum detection

Chromatograms showing manual integration of baselines and spectra (including tentatively identified compounds)

Instrument carry-over between analytical runs.

Validation of ICP should include criteria for evaluating interelement correction factors and how interferences shall be validated.

Additionally, an agreed-upon format to present any trends, in the laboratory or corrective actions taken, that affect sample results should be presented with the data for validation.

8.4 DATA USABILITY

Remember, data are usable if they meet the intended end-use as specified in the DQO process. However, many validation procedures do not address data use. Several important facts need to be understood about many validation and assessment procedures. These facts are as follows.

Method deficiencies may be observed but may not result in data being qualified (flagged as estimated or rejected).

Data may be qualified and still be usable.

Many published validation procedures do not address all aspects of data review.

Examples of method deficiencies not qualified and the data being qualified but usable are presented.

8.4.1 Example 1 – Unqualified Method Deficiencies

Aqueous samples are submitted for analysis for semivolatile organic compounds by Contract Laboratory Program protocol. Two surrogate recoveries in the associated method blank are above the acceptance criteria. The laboratory neglects to re-extract and/or re-analyze the method blank. The associated samples did not contain reportable levels of semivolatile organic compounds and all surrogate recoveries in the samples are within the acceptable criteria. Although the analysis is deficient with respect to the requirements, the data are not qualified and are considered usable.

Samples are submitted for volatile organic compound analysis by 624, 8240, or Contract Laboratory Program protocols. The laboratory inadvertently neglects to analyze a method blank. All other QC requirements are met and target analytes are not detected in any of the samples. Although this is a method deficiency, the data are not qualified. The only intent of a blank is to demonstrate that any detected analytes in project samples are native to the sample and not introduced by the laboratory. When target analytes are not detected, no analytical basis exists for a blank, provided all other QCs meet criteria.

8.4.2 Example 2 -- Data Qualified But Usable

A sample is analyzed for volatile organic compounds and one of the three surrogate recoveries is 1% below the acceptance criterion. Although the data are qualified, the magnitude of the qualification is relatively insignificant with respect to the many other variables impacting data quality. Accordingly, the data for this sample, although qualified, is usable.

A significant number of aqueous samples are analyzed for semivolatile organic compounds by Contract Laboratory Program. All of the samples and the associated field blanks and method blanks reveal levels of phthalate esters at 10 to 15 Φg/L; all other QCs were met. The reported phthalate ester results in samples are qualified because of blank contamination. Although the results are qualified, the analysis for these phthalate esters is usable, provided it is stated that phthalates are not present in samples at concentrations greater than 15 Φg/L.

Once both the laboratory procedures and the validation criteria are in agreement and are agreed upon and documented by the laboratory, the validator, and the client, the samples are submitted for analysis. After analysis and submission of the data to the validator, the laboratory should respond to reasonable queries from the validator regarding the data. The queries and responses should be written.

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9.0 CLARIFICATIONS AND INTERPRETATIONS

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APPENDIX A

SUMMARY OF THE DATA QUALITY OBJECTIVE PLANNING PROCESS

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APPENDIX A

SUMMARY OF THE DATA QUALITY OBJECTIVE PLANNING PROCESS

This appendix summarizes the data quality objective (DQO) planning process. The DQO planning process is a formal method between the laboratory and the client that defines the analytical requirements based on the end-use of data. Participants in the DQO planning process typically include projects engineers, laboratory scientists, sampling and regulatory specialists, a representative of the regulatory community, and a DQO process specialist.

The DQO planning process empowers both clients (which are the data users) and the laboratories (which are the data suppliers) to take control of and resolve vexing issues in a stepwise fashion. The process brings together the clients and the laboratories. Further, the process allows laboratories to be active participants in solving the problems. During this process, the laboratory and the client decide what data shall be needed to make the decision, determine how the data shall be used, and decide the quality control required.

The process consists of seven main steps.

1. Understand the context.
2. State the question(s).
3. Define the potential answer(s).
4. Select the measure(s).
5. Set error tolerances.
6. Establish decision rule(s).
7. Optimize the design.

Table A-1 outlines the steps in the process, the information needed for the DQO planning process, and the information that the laboratory should provide to support the planning process.

Table A-1. Data Needed and Provided by the Laboratory for the Data Quality Objective Planning Process.

Step	Information Needed for the DQO Planning Process	Information Provided by Laboratory
Understand the context	Situation or site history Previous data	N/A
State the question(s)	Issues and problems Any analytes related to the problems	N/A
Define the potential answer(s)	Responses to each question	N/A
Select the measure(s)	Analyte lists Analytes of concern Analytes driving risk Measurement areas Boundaries and areas to sample Matrices Action and regulatory levels	Justification for or against certain analytes Fate and transport information Difficulty of analysis Analytes that serve as indicators for other constituents
Set error tolerances	Allowable difference between the regulatory level and the actual value Needed level of false negative, false positive, or confidence Variability of the sample matrix	Methods potentially used Estimates of the detection levels and variability of the methods
Establish decision rule(s)	The measurement, error tolerance, and decision information combined into logical statements or logic diagrams to allow the decision criteria to be established	N/A
Optimize the design	Sample locations	Methods used to measure analytes

Step	Information Needed for the DQO Planning Process	Information Provided by Laboratory
	Analytes to be measured Action levels Number of samples by matrix Method requirements by regulation	Method detection limits Precision and accuracy by method and analyte Quality control sample types and frequency required, such as method, field, equipment blanks, matrix spikes, and duplicates Sample volume, preservatives, and container requirements

Notes:

DQO = data quality objective.
N/A = not applicable.

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APPENDIX B

U.S. ENVIRONMENTAL PROTECTION AGENCY, CONSENSUS, AND U.S. DEPARTMENT OF ENERGY METHODS

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APPENDIX B

U.S. ENVIRONMENTAL PROTECTION AGENCY, CONSENSUS, AND U.S. DEPARTMENT OF ENERGY METHODS

1.1 U.S. ENVIRONMENTAL PROTECTION AGENCY (EPA)

"Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," SW-846, U.S. Environmental Protection Agency, Washington, D.C.

Contract Laboratory Program and Statement of Work.

For copies of these documents, contact your regional EPA office.

USEPA Methods for Chemical Analysis of Water and Wastes, PB84-128677 (EPA-600/4-79-020, March 83), U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

40 CFR 136, Appendix A, "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater." U.S. Code of Federal Regulations.

Methods for the Determination of Organic Compounds in Drinking Water, PB89-220461 (EPA-600/4-88/039, December 1988), U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, Virginia 22161.

1.2 CONSENSUS

American Public Health Association, American Water Works Association, and Water Pollution Control Federation, *Standard Methods for the Examination of Water and Wastewater* (Standard Methods), American Public Health Association, 1015 15th NW, Washington, D.C. 20005

American Society for Testing Materials (ASTM) methods.

1.3 U.S. DEPARTMENT OF ENERGY (DOE)

DOE Methods for Evaluating Environmental and Waste Management Samples (DOE Compendium), DOE/EM-0089T, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, Virginia 22161.